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SERIES A. VOL. LXXIX.

No. A 527.—March 12, 1907.

OMISSION.

PROCEEDINGS, A. VOL. 79, INDEX.

Insert the following entries:—

No. A 531.—July 10, 1907.

ERRATA.

Page 240, line 25—
    For $T'/T = (p'/p)^{\gamma-1}$ *read* $(T'/T)^{\gamma} = (p'/p)^{\gamma-1}$.

Same page, line 28—
    For   286° C.   *read*   286° Abs.

Same page, line 30—
    For   13½   *read*   39.

On Plate 2 *omit* the note *₊* at foot.

Page 431, fig. 2, curves marked $b = 15$, $b = 20$ should be marked $b = 10$, $b = 15$.

PROCEEDINGS OF

THE ROYAL SOCIETY.

Section A.—Mathematical and Physical Sciences.

Address of the President, Lord Rayleigh, O.M., D.C.L., at the
Anniversary Meeting on November 30, 1906.

Since the last Anniversary the Society has sustained the loss of twelve
Fellows and two Foreign Members.

The deceased Fellows are :—

Professor Lionel Smith Beale, died March 28, 1906.
Sir Walter Lawry Buller, K.C.M.G., died July 19, 1906.
Charles Baron Clarke, died August 25, 1906.
Right Hon. Sir M. E. Grant Duff, G.C.S.I., died January 11, 1906.
Professor Charles Jasper Joly, died January 4, 1906.
Colonel Sir Alexander Moncrieff, K.C.B., died August 3, 1906.
George James Snelus, died June 18, 1906.
Professor Hermann Johann Philipp Sprengel, died January 14, 1906.
General Sir Henry E. L. Thuillier, C.S.I.
Rev. Canon H. B. Tristram, died March 8, 1906.
Professor Harry Marshall Ward, died August 26, 1906.
Professor Walter Frank Raphael Weldon, died April 13, 1906.

The Foreign Members are :—

Professor Ludwig Boltzmann.
Professor Samuel Pierpont Langley.

On this list are to be found the names of veterans distinguished in many
branches of science and in public affairs. One name is a household word in

every physical and chemical laboratory. It would be difficult, indeed, to enumerate the investigations which have owed their success to the invention of the Sprengel mercury pump. In other cases, scientific careers still in full activity have, unhappily, been cut short. I allude especially to Joly, Marshall Ward, and Weldon. Even within my term of office our discussions have been enlivened by Weldon's scientific enthusiasm and vigorous polemics.

On the Foreign list are two distinguished names. Professor Ludwig Boltzmann, of Vienna, was perhaps the first Continental physicist to take up the ideas of Maxwell's electric theory of light, of which he had early grasped the scope and became for many years one of its most emphatic supporters. One of his earliest series of experiments was a determination of the influence of the crystalline quality on the dielectric constant of sulphur, with a view to comparison with its optical double refraction. In the theory of gases he is to be classed along with Clausius and Maxwell as one of the creators of the dynamical theory, on which he became the highest authority. By developing an idea originated by Bartoli he placed Stefan's law of intensity of natural radiation on a theoretical basis, and thus became the pioneer in the modern thermodynamics of radiant energy. He contributed to the advance of physical science by many other investigations, and by his books on Gas Theory, on Electrodynamics, and on Mechanics. I may perhaps be allowed to add that at the time of his unhappy death, Boltzmann's name was before the Council as proposed for one of our medals.

Professor Langley's work was more on the experimental side of physics. In his bolometer he applied electric resistance thermometry to radiation, and was thereby enabled to penetrate further into the important and mysterious region of the ultra-red than had before that time been possible. For this work he received the Rumford Medal in 1886. During the later years of his life his attention was largely occupied with the mechanical problem of flight, and his models attained a considerable measure of success. As Secretary to the Smithsonian Institution at Washington he did much to forward, by his co-operation and advice, all kinds of scientific investigation.

In the Report of the Council there has been laid before you an account of the work of the Council and of various Committees in a very wide field. The investigation of the terrible disease known as Sleeping Sickness has unhappily been marked by the tragic death of Lieutenant Tulloch, who has fallen a victim to his zeal in studying the disease in Uganda. Vigorous efforts are being undertaken to discover some therapeutic remedy for the malady. In the case of Malta Fever, too, the investigation of which was entrusted to the Royal Society by the Colonial Office, good progress has been

made. It has been ascertained by the Society's Commission in Malta that the main source of propagation is the milk of infected goats. When this discovery was made the authorities of the island were at once warned of the danger in the milk supply, and the necessary precautions were taken. Since then the number of cases of fever in the hospitals has so greatly diminished as to afford good hope that this disease, which has been so great a scourge in Malta, may ere long be reduced to insignificant proportions or altogether exterminated.

I observe that a movement has been been started in this country in aid of the Greek Anti-Malaria League. Professor Ronald Ross, than whom there is no higher authority, bears witness to the unexpected prevalence of the infection in most of the localities examined, and he is confident that practical results of the highest value would follow expenditure in combating the disease on lines already laid down. Although I speak only from general knowledge, I cannot let this opportunity pass without emphasising my sense of the enormous importance of this class of work. If men knew where their real interests lie, our efforts in this direction would be doubled or quadrupled. In this way discoveries, which the future will certainly bring, might be accelerated by decades, giving health and life to thousands or millions who now succumb. Willing and competent workers would soon offer themselves; the principal obstacle is the want of means.

The preparation of the 'Royal Society Catalogue of Scientific Papers' for the remaining portion of the 19th century, which has proved a task so much more gigantic than can have been contemplated by the originators of the Catalogue nearly half a century ago, has been actively pushed forward. In consequence of the increased expenditure, now at the rate of nearly £2000 a year, the funds available are again approaching exhaustion. The difficulties of the President and Council and of the Catalogue Committee on this subject have once more been promptly resolved by the action of our Fellow, Dr. Ludwig Mond, who, after consultation with the Officers, has again made himself responsible for a further subsidy amounting to £2000 a year for three years. It is hoped that with the balance in hand and other sources of income, including the Handley Fund of the Royal Society, the income of which is devoted to this purpose, this subvention will suffice for the preparation of the work and for passing it through the press. Since the Royal Society took this great national task in hand there has already been spent on it over £23,500, while on each occasion of financial stress Dr. Mond has come forward with the means of relief, his direct contributions, including that just promised, now amounting in the aggregate to £14,000. This great work when published will thus be a tangible memorial of Dr. Mond's practical insistence on

the importance of adequate indexes of the vastly increasing literature of science.

Of the activities working under the Royal Society the one with which I have been especially connected is the National Physical Laboratory.

In their Report for the past year the Executive Committee call attention to the loss they have sustained by the deaths of Sir Edward Carbutt and Sir Bernhard Samuelson, both members of the Committee and warm supporters of its work.

The Report shows continued progress. As a result of a memorial to the Chancellor of the Exchequer, signed by about 150 Members of Parliament, the Grant for building and equipment for the year was increased from £5000 to £10,000, and this has enabled the Committee to take in hand some urgently needed extension.

Buildings are now in course of erection for Metrology and for Metallurgical Chemistry, while the Engineering Laboratory is being doubled in area. The two last additions were called for in great measure in consequence of an arrangement with the India Office whereby the testing work required for the Indian Government, hitherto carried on at Coopers Hill, is to be transferred to the Laboratory. The Indian Government provide the testing machine and other appliances required for the work, and, in addition, have intimated their intention of placing in the charge of the Committee the very admirable electrical equipment now at Coopers Hill.

Towards the equipment of the Metallurgical Laboratory the Goldsmiths' Company have made a very generous donation of £1000, while the Governments of New Zealand and Western Australia have contributed £100 each to the equipment of the Metrological Laboratory.

The buildings of the Electrical Laboratory have been completed, and were formally opened by the Right Hon. R. B. Haldane in June last. On this occasion many representatives of electrical industry from various parts of the world, who were attending the special conferences of the Institution of Electrical Engineers, were present, and joined in the inspection of the Laboratory.

After the meeting Sir John Brunner announced his intention of subscribing £5000 towards the equipment of the various buildings now in hand.

A number of important researches, a list of which is given in the Report, have been published during the year, and others are in a forward state of preparation for publication. Dr. Carpenter and Mr. Edwards have completed the first part of their research into the properties of the copper-aluminium alloys for the Alloys Research Committee. Dr. Stanton and Mr. Bairstow have read a paper before the Institution of Civil Engineers on

the effect of alternating stresses on steels. The work on electrical standards with the Ampère Balance, which has a special interest for myself, is well advanced. In the hands of Mr. Smith the measurement of the electrolytic deposits of silver, which represent the whole passage of electricity through the apparatus, has attained a remarkable precision and, what is perhaps more important, some anomalies met with at first seem to be on the road to elucidation. Mr. Campbell has made progress with his research on hysteresis in steel sheets, and Dr. Harker is engaged with interesting investigations in high-temperature thermometry.

Changes in the staff have taken place. Dr. Caspari resigned his position in order to take up private practice, while Dr. Carpenter has been appointed the first Professor of Metallurgy in the Victoria University of Manchester. The arrangements with the Indian Government have necessitated an alteration in the metallurgical division, and the Committee have thought it right to constitute a Department of Metallurgy and Metallurgical Chemistry, with a Superintendent in charge of the work. They have been fortunate in securing the services of Mr. W. Rosenhain as the first occupant of the post.

A question of importance has arisen as to the performance at the Laboratory of tests, partaking of a routine character, on the physical and mechanical properties of specimens of material. To this objection has been taken on the ground of competition with the work of private establishments. In one of its aspects the question is financial. But the Executive Committee are of opinion that, even if the pecuniary loss were recouped, the efficiency of the Laboratory would suffer from the abandonment of this work. While anything like unfair competition with private establishments should be avoided, the execution of tests is good practice for the staff, and tends to keep them in touch with the manufacturers and with the practical problems which may demand examination. In view of the difference of opinion that has manifested itself, the Treasury has decided to appoint a small committee to inquire into the working of the Laboratory, with a special reference to this question.

On a former occasion, my distinguished predecessor, Sir William Huggins, called attention to some of the more important matters on which the Society in the past had initiated, supported, or given advice about scientific questions in connection with the State, and in other ways had made its influence felt strongly for the good of the country. It would hardly become me, with my short experience of the working of the Society, at least in recent years, to pursue this theme. The function of the. Society which lies most open to the observation of an incoming President is that exercised at the ordinary meetings. I am impressed with the difficulty, arising out of the ever-

increasing specialisation of science, in rendering really useful the reading of papers and discussions thereupon. It is, of course, felt more severely in a Society like our own, which embraces within its scope the whole scientific field. It not infrequently happens that a paper is addressed to an audience among whom there is no one competent to follow the detailed observations and reasonings of the author. I am sometimes reminded of a saying of Dalton's on similar occasions at Manchester, quoted by Sir Henry Roscoe in his genial and entertaining ' Reminiscences ': " Well, this is a very interesting paper for those that take any interest in it." A little more discretion on the part of readers of papers in having regard to the composition of their actual audience would be helpful here. In some cases experimental illustration would bring home to a larger number what is followed with difficulty from a merely verbal statement. But I am afraid that no complete remedy is within reach.

Increase of specialisation, however inconvenient in some of its aspects, is, I suppose, a necessary condition of progress. Sometimes a big discovery, or the opening up of a new point of view, may supersede detail and bring unity where before there was diversity, but this does not suffice to compensate the general tendency. Even in mathematics, where an outsider would probably expect a considerable degree of homogeneity, the movement towards diversity is very manifest. Those who, like myself, are interested principally in certain departments, and can look back over some 40 years, view the present situation with feelings not unmixed. It is disagreeable to be left too far behind. Much of the activity now displayed has, indeed, taken a channel somewhat remote from the special interests of a physicist, being rather philosophical in its character than scientific in the ordinary sense. Much effort is directed towards strengthening the foundations upon which mathematical reasoning rests. No one can deny that this is a laudable endeavour; but it tends to lead us into fields which have little more relation to natural science than has general metaphysics. One may suspect that when all is done fundamental difficulties will still remain to trouble the souls of our successors. Closely connected is the demand for greater rigour of demonstration. Here I touch upon a rather delicate question, as to which pure mathematicians and physicists are likely to differ. However desirable it may be in itself, the pursuit of rigour appears sometimes to the physicist to lead us away from the high road of progress. He is apt to be impatient of criticism, whose object seems to be rather to pick holes than to illuminate. Is there really any standard of rigour independent of the innate faculties and habitudes of the particular mind? May not an argument be rigorous enough to convince legitimately one thoroughly

imbued with certain images clearly formed, and yet appear hazardous or even irrelevant to another exercised in a different order of ideas? Merely as an example, there are theorems known as "existence-theorems" having physical interpretations, the object of which is to prove formally what to many minds can be no clearer afterwards than it was before. The pure mathematician will reply that even if this be so, the introduction of electrical or thermal ideas into an analytical question is illogical, and from his own point of view he is, of course, quite right. What is rather surprising is that the analytical argument should so often take forms which seem to have little relation to the intuition of the physicist. Possibly a better approach to a reconciliation may come in the future. In the meantime we must be content to allow the two methods to stand side by side, and it will . be well if each party can admit that there is something of value to be learned from the point of view of the other.

In other branches, at any rate, the physicist has drawn immense advantage from the labours of the pure analyst. I may refer especially to the general theory of the complex variable and to the special methods which have been invented for applying it to particular problems. The rigorous solution by Sommerfeld of a famous problem in diffraction, approximately treated by Fresnel, is a case in point. We have moved a long way from the time when it was possible for the highest authority in theoretical optics to protest that he saw no validity in Fresnel's interpretation of the imaginary which presents itself in the expression for the amplitude of reflected light when the angle of incidence exceeds the critical value. In this connection it is interesting to remember that, in his correspondence with Young, Laplace expressed the opinion that the theoretical treatment of reflexion was beyond the powers of analysis. The obvious moral is that we are not to despair of the eventual solution of difficulties that may be too much for ourselves.

As more impartially situated than some, I may, perhaps, venture to say that in my opinion many who work entirely upon the experimental side of science underrate their obligations to the theorist and the mathematician. Without the critical and co-ordinating labours of the latter we should probably be floundering in a bog of imperfectly formulated and often contradictory opinions. Even as it is, some branches can hardly escape reproaches of the kind suggested. I shall not be supposed, I hope, to under-value the labours of the experimenter. The courage and perseverance demanded by much work of this nature is beyond all praise. And success often depends upon what seems like a natural instinct for the truth—one of the rarest of gifts.

MEDALLISTS, 1906.

The Copley Medal is awarded to Professor Elias Metchnikoff, For. Mem. R.S., on the ground of his distinguished services to zoology and to pathology, particularly for his observations on the development of Invertebrates and on phagocytosis and immunity. From 1866 to 1882 Professor Metchnikoff's work was exclusively zoological, and mainly during that period he produced a series of brilliant memoirs dealing with the early development and metamorphoses of Invertebrates.

Although his name stands in the first rank of investigators of these subjects, the most celebrated of his discoveries are those relating to the important part played by wandering mesoderm cells and white blood-corpuscles in the atrophy of larval organs, and in the defence of the organism against infection by Bacteria and Protozoa. It was on these researches that he based his well-known 'Phagocyte Theory.' Metchnikoff's fundamental observations were made in Messina in 1882, and were published in the following year. In these he showed that the absorption and disappearance of the embryonic organs of Echinoderms were effected by wandering mesoderm cells, which devoured and digested the structures which had served their purpose and become effete. The observation that white blood-cells accumulate in an inflamed area after infection by Bacteria suggested that these cells might also devour and thus destroy the invading microbes, and that the process of inflammation was really a physiological and protective reaction of the organism against infection. The study of the infection of *Daphnia* by *Monospora bicuspidata* entirely justified this prediction. The account of the phenomena of infection as seen in this transparent Crustacean was published in 'Virchow's Archiv' (vol. 96) in 1884, while, later in the same year, Metchnikoff published another paper extending these observations to Vertebrates, and showing the universal applicability of his generalisation as to the essential character of the inflammatory process.

During the twenty years which have elapsed since the publication of the 'Phagocyte Theory,' Metchnikoff, with the assistance of a host of pupils and disciples from all parts of the world, has been continuously engaged in the study of the reaction of the organism against infection, and in investigating the essential features of immunity in the light of the illuminating generalisation laid down in 1884.

Though of limited range, and therefore inferior in scientific importance to the more fundamental researches carried out by him previously,

Metchnikoff's recent work on infection by the micro-organism of syphilis and the attainment of protection and immunity against this disease may be mentioned on account of its important practical applications.

It is not too much to say that the work of Metchnikoff has furnished the most fertile conception in modern pathology, and has determined the whole direction of this science during the last two decades.

The Rumford Medal is awarded to Professor Hugh Longbourne Callendar, F.R.S., for his experimental work on heat.

Professor Callendar has devoted his attention chiefly to the improvement of accurate measurement in the science of heat by the application of electrical methods. His first paper " On the Practical Measurement of Temperature," ' Phil. Trans.,' 1887, paved the way for the application of the electrical resistance thermometer to scientific investigation. In a later paper, written in conjunction with Griffiths, " On the Boiling Point of Sulphur, etc.," ' Phil. Trans.,' 1891, the application of his method was further extended, and a simple method of standardisation was proposed. In continuation of this work Professor Callendar has written a number of subsidiary papers dealing with details of construction of instruments, and applications to special purposes. The results of this thermometric work have since been confirmed by Chappuis and Harker, ' Phil. Trans.,' 1889, at the Bureau International, Paris, and by other observers, and are now generally accepted.

More recent developments in accurate electrical thermometry have been described by Professor Callendar in later papers. He has also devised a special type of " gas-resistance " thermometer, depending on the increase of viscosity of a gas with temperature, which is the exact analogue of the electrical resistance thermometer, and possesses peculiar advantages for high-temperature measurements.

The application of electrical resistance thermometers and thermo-couples to the observation of rapid variations of temperature has been utilised by Professor Callendar in the study of the adiabatic expansion of gases and vapours, and in the observations of the cyclical changes of temperature of the steam and of the cylinder walls in a steam-engine. The latter research was undertaken in conjunction with Professor Nicholson, with a view to elucidate the theory of cylinder-condensation.

The researches of Rowland and other experimentalists on the specific heat of water, and the mechanical equivalent of heat, had shown that grave uncertainties affected the value of this most fundamental physical constant, which could not be removed satisfactorily without a complete investigation of the variation of the specific heat of water between 0° and 100° C. Professor

Callendar devised a continuous electrical method of attacking this problem, possessing many important advantages as compared with older methods. He was assisted by Dr. Barnes in carrying out this work, the results of which form the subject of papers by Callendar and Barnes in the 'Phil. Trans. Roy Soc.,' 1901. As an illustration of the probable accuracy of their results it may be observed that, whereas by any of the older formulæ accepted for the variation of the specific heat of water the values of Rowland and of Reynolds and Moorby for the mechanical equivalent are seriously discordant, they are brought into perfect agreement by the work of Callendar and Barnes.

In the subject of conduction of heat Professor Callendar has contributed many original methods described in various minor papers, and, in addition to the thermal investigations with which his name is chiefly associated, has carried out some purely electrical researches.

One of the Royal Medals has been awarded, with the approval of His Majesty, to Professor Alfred George Greenhill, a Fellow of the Society, on account of the number and importance of his mathematical investigations produced between the year 1876 and the present time. They embrace a variety of mechanical and physical subjects, including dynamics, hydromechanics, electricity, and gunnery. He is the author of two treatises on hydromechanics, both remarkable for originality of treatment.

The subject, however, to which he has devoted most time and attention is the theory of elliptic functions. His work on this subject may be placed in two classes: (1) Investigations in which he has extended the subject into new fields, as in the series of memoirs on the " Transformation and Complex Multiplication of Elliptic Functions," contributed to the 'Proceedings of the London Mathematical Society' (vols. 19, 21, 25, 27), and in the memoir on the " Third Elliptic Integral and the Ellipsotomic Problem," in the 'Phil. Trans.' (vol. 203). (2) Applications to Mechanical Problems, mainly dynamical, for purposes of calculation or illustration. In this class may be placed his treatise on the Elliptic Functions, as well as numerous papers in journals and the proceedings of scientific societies.

All Professor Greenhill's work is characterised by much originality, and by a rare power and skill in algebraic analysis.

His Majesty has also approved the award of a Royal Medal to Dr. Dukinfield Henry Scott, also a Fellow of the Society, for his investigations and discoveries in connection with the structure and relationship of fossil plants. Dr. Scott began the very important work which he has accomplished in this subject by helping the late distinguished palæo-

botanist, Professor W. C. Williamson. In this co-operation he greatly enhanced the value of Williamson's work. He not only added many new discoveries, but, what was more important, demonstrated the value of the work in relation to phylogeny.

Dr. Scott has since added much of first-rate importance. He has discovered and elucidated many important types, his work constituting a most valuable acquisition to botany from the evolutionary point of view. It is not only in the accurate investigation of difficult structures that Dr. Scott has been so successful; not the least of his merits lies in the philosophical treatment of the problems suggested by his discoveries. His position as one of the leading palæobotanists in the world is well recognised. He has, both by his personality and by his writings, exercised a well-marked and widespread influence on the work of other botanists. The fact that he has created in this country a vigorous school of palæobotanists may be regarded as an additional claim for the honour now conferred upon him.

The Davy Medal is given to Professor Rudolf Fittig, Professor of Chemistry in the University of Strassbourg, who began to publish scientific work as early as 1858, and in 1864 discovered the method for the synthesis of hydrocarbons homologous with benzene, which has ever since borne his name. Up to about 1880 he worked chiefly on benzene derivatives, but his attention was gradually attracted to the study of lactones and acids, both saturated and unsaturated, which has largely formed the subject of his numerous published papers down to the present day.

Fittig has been a remarkably active worker. The Royal Society Catalogue contains under his name alone 96 papers, and, jointly with students and others, 71 more down to 1883. Since that time a number about equally large has been recorded in the indexes of the chemical journals. The work of Fittig and his students on lactones and acids, and particularly the inter-molecular changes which many unsaturated acids undergo, may be said to be classical, and it has had an important influence on the progress of theoretical chemistry.

The Darwin Medal has been awarded to Professor Hugo de Vries, For. Mem. R.S. Professor de Vries has made a series of important discoveries in connection with the manner in which new races of organisms may originate, and he has materially extended and systematised our knowledge of the laws affecting the results of hybridisation. His work is the outcome of very extensive experiments that have been carried on for many years. He has stimulated numerous investigators, both in Europe and in America,

to extend these enquiries; and the results already obtained are of great importance, both from a theoretical and from a practical point of view. De Vries' work has exercised considerable influence on other branches of biology, and has suggested new lines of investigation in many directions.

Mrs. W. E. Ayrton is the recipient of the Hughes Medal, which is awarded for original discovery in Physical Sciences, particularly electricity and magnetism, or their applications. Her work on the Electric Arc has been described in a paper published in the 'Philosophical Transactions,' and in various other publications.

Mrs. Ayrton's investigations cover a wide area. She discovered the laws connecting the potential difference between the carbons of an arc with the current and with the distance between them, and proved these to apply not only to her own experimental results but to all the published results of previous observers. Dealing with the modifications introduced into the arc by the use of cores in the carbons, she found the causes of these modifications. The peculiar distribution of potential through the arc was traced, and its laws were discovered by her.

Having found the conditions necessary for maintaining a steady arc, and for using the power supplied to it most efficiently, she was able to explain the cause of " hissing," and the causes of certain anomalies in the lighting power of the arc.

For the past four years Mrs. Ayrton has been engaged in investigating the causes of the formation of sand ripples on the seashore.

A Comparison of Values of the Magnetic Elements, deduced from the British Magnetic Survey of 1891, with Recent Observation.

By WILLIAM ELLIS, F.R.S.

In the preparation of maps showing lines of equal magnetic declination for commercial use from the data given in the last great Magnetic Survey of the British Isles* it has of late years become apparent, by comparison with the observations made at the several British Magnetic Observatories of Greenwich, Kew, Stonyhurst, Falmouth, and Valentia, that, owing to decrease in value of the annual variation, the lines, as brought forward from the survey, are now carried too far to the west, that is to say, they give a value of declination that is too small, the discordance being apparently greater towards the west than on the eastern side. I have thus thought that it would be desirable to examine this question further, not only for declination, but also for horizontal force and dip, comparing the survey values as brought forward to the epoch 1906·0 by use of the annual rates of change which obtained when it was made with the results of recent observation at the places mentioned.

It will be interesting, in the first instance, to ascertain in what degree the annual variation of the several elements may have changed in recent times. This is shown in Table I, which gives the mean annual variation of each

Table I.—Annual Variation of Magnetic Elements in Three Successive Periods.

Period.	Declination.			Horizontal force.			Dip.		
	Green-wich.	Kew.	Stony-hurst.	Green-wich.	Kew.	Stony-hurst.	Green-wich.	Kew.	Stony-hurst.
1871—1891	−6′·9	−7′·4	−7′·8	+20	+19	+18	−1′·4	−1′·2	−1′·2
1891—1901	−5·7	−5·3	−5·1	+23	+26	+26	−1·7	−2·4	−2·0
1901—1905	−4·0	−4·0	−4·0	+10	+15	+16	−2·5	−1·4	−1·1
Magnetic survey	−6·2	−6·3	−6·9	+20	+20	+20	−1·3	−1·3	−1·2

The unit in horizontal force is 0·0001 of the value in metrical measure = 1·82 approximately.

* "A Magnetic Survey of the British Isles for the Epoch January 1, 1891," by A. W. Rücker, M.A., F.R.S., and T. E. Thorpe, D.Sc., LL.D., F.R.S., 'Phil. Trans.,' vol. 188.

element at Greenwich, Kew, and Stonyhurst in three successive periods, the values in the last period being those appearing in Table II, adding thereto corresponding information from Table XIV of the magnetic survey.

Remarking that the survey values appear to have been deduced mainly from a consideration of the period 1886 to 1891, the epochs of the first and second survey, without knowledge of what might happen after 1891, the survey values appear to be generally well in accord with other observations. We see, however, what has followed in declination: a rapid continuous numerical decrease in magnitude of the annual variation at all three stations. But in horizontal force there is definite increase of value in the second period at all stations, with drop of value in the third period to something less than the values of the first period. In dip there is marked numerical increase of value in the second period at Kew and Stonyhurst, with reversion in the third period to values more in accord with those of the first period. At Greenwich there is only a small increase in the second period, with a considerable increase in the third period, an increase that would appear to be real, although opposed to what occurred at Kew and Stonyhurst, since the yearly value at Greenwich depends on five or six observations each of two needles in every month, the difference between the resulting means of the two needles in 1901, 1902, 1903, and 1904 being only 0'·1, 0'·0, 0'·3, and 0'·2 respectively. Of that in 1905 I have no information.

Extracting now from the various official publications* the mean yearly values of declination, horizontal force, and dip for the years 1901 to 1905, values which apply to the middle of each year, the mean of these five values is taken for each element at each place, thus giving values that apply to the epoch 1903·5 as appearing in Column (2) of Table II. The difference between the first and last of the yearly values (1901 and 1905), divided in each case by four, is taken as the annual variation,† excepting for horizontal force at Stonyhurst and Falmouth, and dip at Stonyhurst, which, on account of some little irregularity in the progression of the yearly values, were treated graphically, extending the series a little backward, so producing values for the period 1901 to 1905 that were sufficiently satisfactory. The resulting annual variations are given in Column (3). In Column (4) the observed values

* 'Results of the Magnetical and Meteorological Observations made at the Royal Observatory, Greenwich'; 'Report of the Observatory Department of the National Physical Laboratory'; 'Results of Meteorological and Magnetical Observations at Stonyhurst College Observatory.'

† The determination of annual variation from observations made at a particular hour of the day (instead of from mean values), as at Stonyhurst and Valentia, is not strictly accurate, but is abundantly so for the purposes of this paper.

of Column (2) are reduced to the epoch 1906·0 by the annual variations of Column (3). The values are mean values. To secure this, however, as the observations of declination, horizontal force, and dip at Stonyhurst were made at 16 h., 10 h., and 12 h. respectively (civil time counting from midnight), and at Valentia at 10 h., 12 h., and 13 h. respectively, small corrections* to reduce to mean values became necessary, as shown in Table II. The Greenwich values of dip also were made on the average from 13 h. to 14 h., and the Falmouth observations in 1901, 1902, and 1903 at 15 h., but no corrections for diurnal range were in these cases necessary.

It becomes of interest here to note that the Greenwich values of declination include all days, excepting those of great magnetic disturbance, whilst the Kew and Falmouth declinations include only the five selected quiet days in each month, and further to inquire whether the declinations found by these two methods show any difference. The declinations at Greenwich were therefore calculated for the years 1903 and 1904, including only the five quiet days in each month, with the following result :—

Greenwich Magnetic Declination.

	Including all days.	Including quiet days only.	Excess of latter.
1903	16° 19'·1	16° 19'·2	+ 0·1
1904	16° 15'·0	16° 14'·9	− 0·1

As regards the difference between the separate monthly values in the 24 months of the two years, on three occasions there was no difference, on five occasions a difference of 0'·1, on eleven occasions 0'·2, on two occasions 0'·3, and 0'·4, 0'·5, and 0'·6 on one occasion each only. In horizontal force the result would be presumably similar.

Coming now to the survey values, Column (5) of Table II contains the value of each element, at each place, for 1891·0 from Table XXIV of the Magnetic Survey, reduced to the epoch 1906·0 by means of the annual variations of Table XIV. But as survey values for Greenwich for 1891·0 do not appear in Table XXIV, they have been calculated from Tables XX, XXI, and XXII, and similarly brought forward to 1906·0 by the survey variations. To these values, by application of the local deviation (difference between the observed and survey values for 1891·0 in Table XXIV), the concluded survey values for 1896·0 are found, the difference between which and the observed values for the same epoch (Column (4)) showing the discordance of the survey value. The survey values for Greenwich not having

* From a consideration of the records at Greenwich, Kew, and Falmouth, 1901 to 1905.

been inserted in Table XXIV, the difference between those specially calculated for 1891·0, as above mentioned (declination 17° 18'·8, horizontal force 1·8241, dip 67° 24'·7), and the observed Greenwich values for 1891·0 (declination 17° 26'·0, horizontal force 1·8242, dip 67° 23'·9) have been for this purpose taken as the local deviation. The resulting comparison is shown in Table II.

Table II.—Comparison of Magnetic Survey Values of Declination, Horizontal Force, and Dip, reduced to the Epoch 1906·0, with Results derived from Direct Observation.

(1) Place of observation.	(2) Observed value 1903·5.	(3) Annual variation.	(4) Reduced to 1906·0.	(5) Survey value reduced to 1906·0.	(6) Local deviation.	(7) Concluded survey value 1906·0.	(8) Discordance of the survey value.
Greenwich	16° 18'·6	−4'·0	16° 8'·6	15° 45'·8	+ 7'·2	15° 53'·0	−15·6
Kew	16 41 ·0	−4 ·0	16 31 ·0	15 53 ·3	+15 ·9	16 9 ·2	−21 ·8
Stonyhurst	18 1 ·5	−4 ·0	17 50 ·0[1]	17 28 ·3	− 8 ·4	17 19 ·9	−30 ·1
Falmouth	18 17 ·1	−4 ·3	18 6 ·4	17 30 ·7	+ 3 ·6	17 34 ·3	−32 ·1
Valentia	21 19 ·2	−4 ·3	21 9 ·5[2]	20 31 ·4	+ 0 ·3	20 31 ·7	−37 ·8
Greenwich	1 ·8507	+0 ·0010	1 ·8532	1 ·8538	+0 ·0001	1 ·8539	+0 ·0007
Kew	1 ·8486	+0 ·0015	1 ·8523	1 ·8526	−0 ·0019	1 ·8507	−0 ·0016
Stonyhurst	1 ·7367	+0 ·0016	1 ·7422[3]	1 ·7423	+0 ·0007	1 ·7430	+0 ·0008
Falmouth	1 ·8745	+0 ·0015	1 ·8783	1 ·8836	−0 ·0041	1 ·8795	+0 ·0012
Valentia	1 ·7831	+0 ·0012	1 ·7876[4]	1 ·7813	+0 ·0068	1 ·7831	+0 ·0005
Greenwich	67° 0'·7	−2'·5	66° 54'·4	67° 5'·8	−0'·8	67° 5'·0	+10·6
Kew	67 6 ·6	−1 ·4	67 3 ·1	67 7 ·6	+4 ·9	67 12 ·5	+ 9 ·4
Stonyhurst	68 47 ·2	−1 ·1	68 43 ·9[5]	68 53 ·2	−1 ·3	68 51 ·9	+ 8 ·0
Falmouth	66 39 ·1	−1 ·7	66 34 ·9	66 47 ·0	−2 ·0	66 45 ·0	+10 ·1
Valentia	68 22 ·6	−1 ·8	68 17 ·9[6]	68 30 ·5	−5 ·5	68 25 ·0	+ 7 ·1

Corrections for diurnal range are included—in (1),−1'·5 ; in (2),+1'·0; in (3) and (4),+0·0015 ; in (5), −0'·5; in (6), −0'·2.

The horizontal force is in metrical measure.

The survey values for declination, brought up to the present time, thus give a westerly declination that is too small as compared with observation, the difference being greatest on the western side, and the dip, similarly brought up, gives a value that is too great, with little difference in amount at the various places. The survey values of horizontal force are in much closer agreement with observation.

The discordance in horizontal force is expressed in metrical measure, but in order to show the relative magnitude of the discordances in the other elements of declination and dip, these have been converted also into metrical

measure at each station by means of the data contained in Table II, the factor for declination expressed in minutes being, horizontal force metric × sin 1′, and that for dip, total force metric × sin 1′, the values of horizontal force at the different stations ranging from 1·7422 at Stonyhurst to 1·8783 at Falmouth, and that of total force ranging from 4·7235 at Greenwich to 4·8347 at Valentia. These results are given in Table III :—

Table III.—Discordances of Survey Values in Metrical Measure
(unit = 0·0001 of the metrical values of horizontal force and total force respectively).

Station.	Latitude North.	Longitude West.	Declination.	Horizontal force.	Dip.
	° ′	° ′			
Greenwich	51 29	0 0	− 84	+ 7	+146
Kew	51 28	0 19	−117	−16	+130
Stonyhurst	53 51	2 28	−153	+ 8	+112
Falmouth	50 9	5 5	−175	+12	+139
Valentia	51 56	10 15	−197	+ 5	+100
Approximate value in metrical measure				1·82 Horizontal force.	4·77 Total force.

The discordances thus pointed out have no concern with the important deductions and conclusions regarding the magnetic condition of the British Isles, so fully discussed in the survey volume, but simply indicate that the secular variations of Table XIV of the survey have undergone change since the time when the survey was made, especially in the case of magnetic declination and dip. The secular changes there tabulated were primarily put together for the necessary purpose of reducing the observations on which the survey was based to a mean epoch, and were not intended for application to future years without being checked. As the authors of the survey pointed out, the continuous records available at the various magnetic observatories, combined with further magnetic observations, taken from time to time, at a limited number of selected stations distributed over the area covered by the survey, may give sufficient information, the local deviations being thus known, for rectification of the mean lines of equal values of the several magnetic elements.

On the Intensity of Light Reflected from Transparent Substances.

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A careful comparison of theory with experiment as regards the intensity of reflection would seem to suggest itself naturally as a crucial test of the validity of any optical theory. In spite of this, it was not till late in the last century that the problem was seriously undertaken by experimentalists. In 1870 Rood* turned his attention to the subject with the view of testing Fresnel's laws, and concluded from his experiments "that the reflecting power of glass conforms, in the closest manner, to the predictions of theory." However, in 1886, this conclusion was shown to be untenable by Lord Rayleigh.† The difficulties of measuring the intensity of the reflected light accurately are very considerable, and Rood had contented himself with estimating the transmitted light and deducing the amount that was reflected. Rayleigh showed that when this fact was considered the difference between Fresnel's formula and Rood's experimental results might amount to 7 per cent. of the reflected light, a difference much too great to be regarded as insignificant. Rayleigh found from his own experiments that recently polished glass has a reflecting power differing not more than 1 or 2 per cent. from Fresnel's formula; but that after some months or years the reflection may fall off 10 per cent. or more, and that without any apparent tarnish. About the same time Sir John Conroy carried out a lengthy series of experiments on the same subject. His results were published in the 'Phil. Trans.,' 1888, and confirmed those of Lord Rayleigh.

There can thus be no doubt of a decided departure from Fresnel's formula under certain circumstances. The difference is too great to be put down to experimental errors, and there is no evidence of such errors, seeing that the results of experiment are fairly consistent. Nor can there be very much doubt as to the direction in which to look for an explanation of the apparent divergence between theory and experiment. Everything points to a changing condition of the reflecting surface, and this suggests that a consideration of the layer of transition will show how Fresnel's laws are departed from in this as in some other directions. The object of the present paper is to investigate

* 'Amer. Journ. Science,' vols. 49 and 50.
† 'Roy. Soc. Proc.,' vol. 41; 'Scientific Papers,' vol. 2, p. 522.

this matter rather more systematically than appears to have been done hitherto.

In the first place it will be convenient to estimate the influence on the reflective power at normal incidence of a *uniform* layer on the surface of the reflecting substance. Let p be the frequency, c the velocity of light, and λ the wave-length in air, μ the refractive index of the reflecting substance, μ' that of the layer, and d its thickness. In the layer the components of the light vector are proportional to $e^{ip(t-\mu'z/c)}$. Hence a wave of unit amplitude will become of amplitude q after traversing the layer, where $q = e^{-ip\mu'd/c}$.

Thus,

$$q^2 = e^{-i\theta}, \quad \text{where} \quad \theta = 2p\mu'd/c = 4\pi\mu'd/\lambda = 2\mu'd_1, \quad \text{where} \quad d_1 = 2\pi d/\lambda.$$

If r_1 and r_2 be the factors of reflection on passing from air to the layer (μ') and from the layer to the reflecting substance (μ) respectively, then the reflected beam is represented by $\dfrac{r_1 + q^2 r_2}{1 + q^2 r_1 r_2}$, where $q^2 = e^{-i\theta}$.

Hence if I be the intensity of the reflected light, we have

$$\mathrm{I} = \frac{r_1^2 + r_2^2 + 2r_1 r_2 \cos\theta}{1 + r_1^2 r_2^2 + 2r_1 r_2 \cos\theta}, \quad \text{so that} \quad \cos\theta = \frac{\mathrm{I}(1 + r_1^2 r_2^2) - (r_1^2 + r_2^2)}{2r_1 r_2(1 - \mathrm{I})}.$$

The values of r_1 and r_2 are given by Fresnel's formula, viz., $r_1 = \dfrac{\mu' - 1}{\mu' + 1}$, $r_2 = \dfrac{\mu - \mu'}{\mu + \mu'}$. If the thickness of the layer be so small that the *square* of d_1 can be neglected, then $\cos\theta = 1$ and $\mathrm{I} = \left(\dfrac{r_1 + r_2}{1 + r_1 r_2}\right)^2$.

From the values of r_1 and r_2 given above we easily obtain

$$\frac{r_1 + r_2}{1 + r_1 r_2} = \frac{\mu - 1}{\mu + 1}.$$

In this case, then, $\mathrm{I} = \left(\dfrac{\mu - 1}{\mu + 1}\right)^2$, which is the value of the intensity if there is no layer. It thus appears, as is to be expected for general reasons, that an exceedingly thin layer of transparent matter produces no effect on the intensity of the reflected light, and that in any case where a change is observed the thickness of the layer must be such that the square of $2\pi d/\lambda$ is appreciable.

If κ be the intensity when there is no layer, and if the layer diminishes the intensity by $1/n$, then we have

$$\mathrm{I} = \kappa\left(1 - \frac{1}{n}\right) \quad \text{and} \quad \frac{r_1 + r_2}{1 + r_1 r_2} = \sqrt{\kappa}.$$

Hence

$$\cos\theta = \frac{\kappa(1-n^{-1})(1+r_1^2 r_2^2)-(r_1+r_2)^2+2r_1 r_2}{2r_1 r_2(1-\kappa+\kappa n^{-1})}$$

$$= \frac{1-\kappa-\frac{1}{2}\kappa n^{-1}(r_1 r_2+r_1^{-1} r_2^{-1})}{1-\kappa+\kappa n^{-1}}.$$

To obtain the minimum value of θ we have to make $r_1 r_2+(r_1 r_2)^{-1}$ a minimum. Now $r_1 r_2$ vanishes when $\mu'=1$ and when $\mu'=\mu$, and r_1 and r_2 are both fractions, so that $r_1 r_2$ is always less than unity. Thus we cannot have $r_1 r_2 = 1$, which would make $r_1 r_2+(r_1 r_2)^{-1}$ a minimum. But we also get a minimum value of θ by making $r_1 r_2$ a maximum. This makes $\mu'^2=\mu$ and $r_1 = r_2 = (\sqrt{\mu}-1)/(\sqrt{\mu}+1)$. This enables us to estimate approximately what must be the refractive index of the layer in order to produce a given diminution of intensity with the thinnest possible layer. We have $2\pi d/\lambda = d_1 = \theta/2\mu'$, and as θ is a minimum when $\mu' = \sqrt{\mu}$, we see that d will be a minimum for a value of μ' rather greater than $\sqrt{\mu}$. This result is independent of the thickness of the layer, but if this is not large a simple formula for the value of μ' that makes d a minimum is easily found.

We have

$$\cos 2\mu' d_1 = \cos\theta = \frac{1-\kappa-\frac{1}{2}\kappa n^{-1}(r_1 r_2+r_1^{-1} r_2^{-1})}{1-\kappa+\kappa n^{-1}}.$$

Hence if d_1 be a minimum, we must also have

$$d_1 \sin 2\mu' d_1 = \frac{\kappa(\mu+1)}{2n(1-\kappa)+2\kappa} \frac{\mu-\mu'^2}{(\mu'^2-1)(\mu^2-\mu'^2)}(r_1 r_2-r_1^{-1} r_2^{-1}).$$

These equations may be written

$$\left(1-\kappa+\frac{\kappa}{n}\right)\cos\theta = 1-\kappa-\frac{\kappa}{n}\frac{\mu'^4+\mu'^2(\mu^2+4\mu+1)+\mu^2}{(\mu'^2-1)(\mu^2-\mu'^2)}, \qquad \text{(i)}$$

and $\qquad \left(1-\kappa+\frac{\kappa}{n}\right)\theta \sin\theta = -\frac{4\kappa}{n}\cdot\frac{(\mu+1)^2(\mu^2-\mu'^4)\mu'^2}{(\mu'^2-1)^2(\mu^2-\mu'^2)^2}. \qquad \text{(ii)}$

Now if we neglect *fourth* and higher powers of θ, we have $\cos\theta = 1-\frac{1}{2}\theta\sin\theta$, and substituting in (i) and (ii), we get

$$1-\kappa-\frac{\kappa}{n}\left[\frac{\mu'^4+\mu'^2(\mu^2+4\mu+1)+\mu^2}{(\mu'^2-1)(\mu^2-\mu'^2)}\right] = 1-\kappa+\frac{\kappa}{n}+\frac{2\kappa}{n}\cdot\frac{(\mu+1)^2\mu'^2(\mu^2-\mu'^4)}{(\mu'^2-1)^2(\mu^2-\mu'^2)^2},$$

which reduces to $\qquad\qquad \mu'^4[\mu^2+1-2\mu'^2] = 0$,

so that the layer is thinnest when $\mu'^2 = \frac{1}{2}(\mu^2+1)$.

To illustrate the relation between the refractive index and the thickness of the layer required to effect a given diminution of the intensity, we have the following table, in which $\mu = 1.5$ and the intensity is diminished 10 per cent. by the layer.

μ'.	1·1	1·2	1·225	1·25	1·275	1·3	1·4
d_1	0·3563	0·2749	0·2676	0·2637	0·2624	0·2643	0·3153

The thickness is least when $\mu = \sqrt{\tfrac{1}{2}(1+\mu^2)} = 1\cdot275$. For sodium light this would make the thickness of the layer rather less than 1/10000 of an inch.

This investigation of the influence of a uniform layer on the intensity shows that the value of d_1 required to produce a diminution of intensity such as was observed by Rayleigh and Conroy is not large. The hypothesis of a uniform layer in the cases dealt with by these experimenters is highly improbable, it being much more reasonable to suppose that there is a layer of gradual transition from one medium to the other. To investigate completely the effect of such a layer in the most general case would be a very trouble-some matter, even if the law of variation of the refractive index were known—which is, of course, not the case. The problem, however, becomes comparatively simple* when the thickness of the layer is such that we can proceed by successive approximations, retaining different powers of d_1. The investigation of the simple case of a uniform layer suggests that this method is legitimate. The value of d_1 for a layer of gradual transition might be expected to be rather larger than for a uniform layer; but as d_1 for the uniform layer is little greater than 1/4, we should expect it to be considerably less than unity for the transition layer. The sequel will prove that this expectation is well founded and will justify the method of procedure.

We have already seen that for a layer of transparent matter it will be necessary to retain terms of the second order in d_1. The formulæ for such a case are given on pp. 59 and 60 of the paper just referred to.

If ϕ be the angle of incidence, μ the index of refraction, and $\sin \phi = \mu \sin \phi'$ then—except very near the polarising angle—the amplitude of the reflected wave for vibrations parallel to the plane of incidence is given by the formula

$$R = \frac{\mu \cos \phi - \cos \phi'}{\mu \cos \phi + \cos \phi'}\left[1 + \frac{2 \cos \phi \cos \phi'}{(\mu^2 \cos^2 \phi - \cos^2 \phi')^2}(a + b \sin^2 \phi + c \sin^4 \phi)\right].$$

Similarly, for vibrations perpendicular to the plane of incidence we have

$$R' = \frac{\mu \cos \phi' - \cos \phi}{\mu \cos \phi' + \cos \phi}\left[1 + \frac{2a \cos \phi \cos \phi'}{(\mu^2 \cos^2 \phi' - \cos^2 \phi)^2}\right],$$

* See 'Roy. Soc. Proc.,' A, vol. 76, 1905, p. 49.

where

$$a = \mu^3 d_1^2 \left[E^2 \mu^2 + 1 - 2E - 2H (\mu^2 - 1) \right],$$

$$b = \mu^3 d_1^2 \left[-E^2 (1 + \mu^2) - 2 (F - E) \mu^{-2} + EF (1 + \mu^2) \mu^{-2} - (L - J)(1 - \mu^{-2}) \right.$$
$$\left. + 2H (\mu^2 - \mu^{-2}) \right],$$

$$c = \mu^3 d_1^2 \left[E^2 + F^2 \mu^{-4} - EF (1 + \mu^{-4}) + (L - J)(1 - \mu^{-4}) \right].$$

The addition to the intensity due to the layer is

$$2 \cos \phi \cos \phi' \left[\frac{a + b \sin^2 \phi + c \sin^4 \phi}{(\mu \cos \phi + \cos \phi')^4} + \frac{a}{(\mu \cos \phi' + \cos \phi)^4} \right];$$

so that, as far as the correction to the intensity is concerned, everything can be expressed in terms of *three* constants a, b, and c, depending on the thickness of the layer and the law of distribution of μ' within the layer. At normal incidence the correction is $2a/(\mu + 1)^4$, and this will be positive or negative according to the sign of a, that is, according as H is less or greater than $(E^2 \mu^2 + 1 - 2E)/2(\mu^2 - 1)$.

In order to test these results, we shall compare them with Conroy's experiments[*] on the amount of light reflected by Crown glass (before repolishing) at various incidences.

On plotting Conroy's results, it is seen that they are very fairly consistent, except that the mean of his measurements at 40° is somewhat high, and that at 70° rather low. This is probably due to the fact that his estimate of the intensity of reflection at these two angles was made under different circumstances than at most of the other incidences. In most cases he made experiments with his photometer in two positions (A and B), and at 50°, 60°, and 65° the B readings are uniformly higher than the A ones. If we assume that the same would have been the case at 40° and 70°, we shall have to depress his result at 40° in a certain ratio, and raise that at 70°, for at the former angle the readings were all in the position B, and at the latter in the position A.

The value of μ was found by Conroy to be 1·5145. For the other constants a, b, and c appearing in the expression for the intensity, and due to the presence of the layer, we shall take tentatively—

$$a = -0·041, \quad b = 0·06642, \quad c = -0·08079.$$

With these we derive the following table, giving the intensity of reflection at different angles of incidence, and a comparison with the results of Conroy's experiments:—

* 'Phil. Trans.,' A, vol. 180, p. 271.

φ =	0.	10°.	20°.	30°.	40°.	50°.	60°.	65°.	70°.
Theory	0·0378	0·0378	0·0380	0·0392	0·0439	0·0537	0·0831	0·1128	0·1612
Experiment ...	0·0378	0·0378	0·0377	0·0392	0·0437	0·0553	0·0854	0·1116	0·1604
Difference ...	0	0	+0·0003	0	+0·0002	−0·0016	−0·0023	+0·0012	+0·0008

In this table the experimental results at 40° and 70° have been
"corrected" in accordance with the principle explained above. The results
are exhibited graphically in fig. 1 below, and it will be seen from this figure,
or from the table above, that the agreement between theory and experiment is as
close as could be desired. The continuous curve corresponds to the theory,
the crosses represent the experimental results.

Fig. 1.
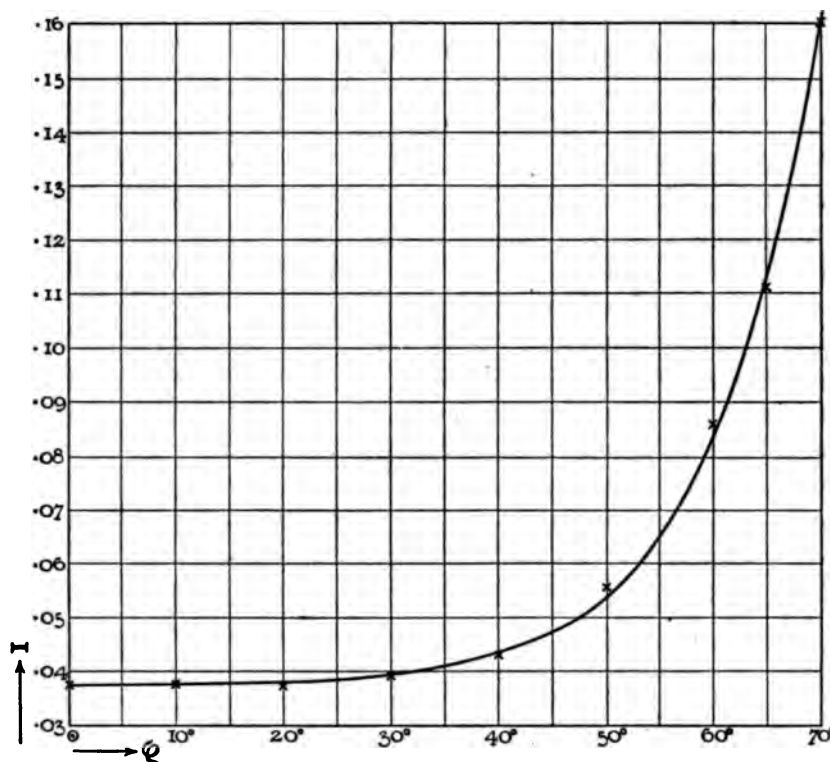
We have seen that if we are concerned only with the intensity of the
reflected light, everything can be determined satisfactorily in terms of three
constants *a*, *b*, and *c*. If, however, we wish to discuss all the circumstances
of the case, *i.e.*, not merely the intensity of the reflected light, but also the
position of the polarising angle, the change of phase produced by reflection,

and the amplitude and phase of the transmitted beam, then there are six constants concerned—d_1, E, F, H, J, and L.   All of these, except d_1, could be calculated by integration for a given law of refractive index (μ') within the layer.

The converse problem of determining the law of μ' to fit in with the experimental results of any given case is, of course, indeterminate. Theoretically we might obtain a number of terms in the expression of μ'^2 by taking, in the most general case,

$$\mu'^2 = (1+p_1x)(1+p_2x)(1+p_3x)(1+p_4x)(1+p_5x)(1+p_6x).$$

The integrations involved in the calculation of E, F, H, J, and L could all be carried out, and a comparison of theory with the experimental measure of six different quantities would give sufficient equations to determine the unknown constants p.   It is obvious, however, that the algebraical equations thus obtained would be very complicated, if not quite intractable.   If we wish to form some estimate of the law of variation of the refractive index within the layer, it will probably be much simpler to calculate the constants for various simple laws in the hope of reaching one that fits in well with the facts.

As an example of this method, and to see in what way the various constants depend on the law of μ' within the layer, we shall consider the case presented by Conroy's experiments now under discussion.   If the layer is of thickness d_2 we shall regard it as extending from $x=0$ to $x=1$, so that xd is the distance of a point from one boundary of the layer.[*]   The various constants will be determined for different laws of μ', *e.g.*, for $\mu'^2=1+px$, the constant p being chosen in each case so as to make $\mu'=\mu=1{\cdot}5145$ at the boundary of the layer where $x=1$.   In order to give results agreeing with experiment when the incidence is normal, we must take the constant $a=0{\cdot}041$.   This will determine the thickness of the layer (d) and the quantity d_1 ($=2\pi d/\lambda$), in each case, in virtue of the formula for a on p. 22 above.   The results are set out in the following table :—

	μ'^2.	p.	E.	H.	F.	J.	L.	$+b$.	$-c$.	d_1.
I	$1+px$	μ^2-1	0·7178	0·3120	1·472	0·3886	0·6679	0·06512	0·06958	0·4386
II	$1/(1+px)$	$1/\mu^2-1$	0·6415	0·2770	1·647	0·3886	0·6679	0·06971	0·07665	0·4606
III	$1+px^2$	μ^2-1	0·6240	0·2650	1·714	0·3805	0·6885	0·03859	0·07718	0·5406
IV	$1/(1+px^2)$	$1/\mu^2-1$	0·5661	0·2455	1·863	0·3975	0·6570	0·1201	0·08175	0·6039
V	$(1+px)^{\frac{1}{2}}$	μ^4-1	0·7546	0·3320	1·393	0·3950	0·6570	0·06527	0·06579	0·4341
VI	$(1+px)^{-\frac{1}{2}}$	$1/\mu^4-1$	0·6071	0·2637	1·732	0·3950	0·6570	0·06642	0·08079	0·4810
VII	$(1+px^2)^{\frac{1}{2}}$	μ^4-1	0·6554	0·2780	1·636	0·3770	0·6949	0·03281	0·07381	0·5135
VIII	$(1+px^2)^{-\frac{1}{2}}$	$1/\mu^4-1$	0·5419	0·2382	1·926	0·4070	0·6362	0·03599	0·08921	0·6655
IX	$(1+px)^2$	$\mu-1$	0·6987	0·3024	1·5145	0·3868	0·6714	0·1341	0·08569	0·4863

[*] Compare 'Roy. Soc. Proc.,' A, vol. 76, 1905, p. 53.   What is there denoted by x_1 is here called x.

With the values of the constants a, b, and c derived from this table we can calculate the intensity of the light reflected at different incidences for the various laws considered. The following table exhibits the results of this calculation :—

$\phi =$	0.	10°.	20°.	30°.	40°.	50°.	60°.	65°.	70°.
I	0·0378	0·0378	0·0380	0·0392	0·0430	0·0540	0·0838	0·1138	0·1626
II	0·0378	0·0378	0·0380	0·0392	0·0431	0·0541	0·0837	0·1137	0·1621
III	0·0378	0·0378	0·0378	0·0387	0·0421	0·0523	0·0806	0·1096	0·1571
IV	0·0378	0·0379	0·0383	0·0400	0·0446	0·0568	0·0884	0·1196	0·1699
V	0·0378	0·0378	0·0380	0·0392	0·0431	0·0541	0·0841	0·1142	0·1632
VI	0·0378	0·0378	0·0380	0·0392	0·0439	0·0537	0·0831	0·1128	0·1612
VII	0·0378	0·0378	0·0378	0·0388	0·0429	0·0520	0·0803	0·1092	0·1567
VIII	0·0378	0·0378	0·0378	0·0387	0·0428	0·0517	0·0795	0·1080	0·1550
IX	0·0378	0·0379	0·0384	0·0402	0·0450	0·0575	0·0875	0·1210	0·1725

The differences between these results and those of Conroy's experiments are as follows :—

$\phi =$	0.	10°.	20°.	30°.	40°.	50°.	60°.	65°.	70°.
I	0	0	+0·0003	0	−0·0007	−0·0013	−0·0016	+0·0022	+0·0022
II	0	0	+0·0003	0	−0·0006	−0·0012	−0·0017	+0·0021	+0·0017
III	0	0	+0·0001	−0·0005	−0·0016	−0·0030	−0·0048	−0·0020	−0·0033
IV	0	+0·0001	+0·0006	+0·0008	+0·0009	+0·0015	+0·0030	+0·0080	+0·0095
V	0	0	+0·0003	0	−0·0006	−0·0011	−0·0013	+0·0026	+0·0028
VI	0	0	+0·0003	0	+0·0002	−0·0016	−0·0023	+0·0012	+0·0008
VII	0	0	+0·0001	−0·0004	−0·0008	−0·0033	−0·0051	−0·0024	−0·0087
VIII	0	0	+0·0001	−0·0005	−0·0009	−0·0036	−0·0059	−0·0036	−0·0054
IX	0	+0·0001	+0·0007	+0·0010	+0·0013	+0·0022	+0·0041	+0·0094	+0·0121

An examination of this table shows that Law VI, according to which $\mu'^2 = (1 + px)^-$, agrees best with the experimental results, and this is the case represented in fig. 1 above. It will be seen, however, that some of the other laws, e.g., I and II, represent the intensity almost equally well. There are, however, other quantities than the intensity of the reflected light that have to be considered. One of these, recorded by Conroy, is the magnitude of the polarising angle. This will depend on the law of variation of μ' within the layer, and we shall proceed to obtain a formula setting out the nature of this dependence.

For vibrations parallel to the plane of incidence we have the following formula for r, the vector representing the reflected beam :—[*]

$$r = \frac{(\mu \cos \phi - \cos \phi') + i\mu d_1 (E\mu \cos \phi \cos \phi' - 1 + F\mu^{-2} \sin^2 \phi)}{(\mu \cos \phi + \cos \phi') + i\mu d_1 (E\mu \cos \phi \cos \phi' + 1 - F\mu^{-2} \sin^2 \phi)} .$$

[*] See 'Roy. Soc. Proc.,' A, vol. 76, 1905, p. 55.

At Brewster's angle we have $\mu \cos \phi - \cos \phi' = 0$, so that in its neighbourhood the intensity of the reflected light is

$$I = |r|^2 = \left(\frac{\mu \cos \phi - \cos \phi'}{\mu \cos \phi + \cos \phi'}\right)^2 + \mu^2 d_1^2 \left(\frac{E\mu \cos \phi \cos \phi' - 1 + F\mu^{-2} \sin^2 \phi}{\mu \cos \phi + \cos \phi'}\right)^2$$

$$= R^2 + \rho^2,$$

where

$$R = \frac{\mu \cos \phi - \cos \phi'}{\mu \cos \phi + \cos \phi'} \quad \text{and} \quad \rho = \mu d_1 \frac{E\mu \cos \phi \cos \phi' - 1 + F\mu^{-2} \sin^2 \phi}{\mu \cos \phi + \cos \phi'}.$$

The intensity is a minimum when $R\frac{dR}{d\phi} + \rho\frac{d\rho}{d\phi} = 0$; now, $\rho\frac{d\rho}{d\phi}$ is of the *second* order of small quantities, so that if we neglect terms of this order we have $R(dR/d\phi) = 0$, which is satisfied by $R = 0$, *i.e.*, $\mu \cos \phi - \cos \phi' = 0$. This gives $\phi = \alpha = \tan^{-1}\mu$, *i.e.*, Brewster's angle, so that, to the first order of small quantities, the layer has no influence on the position of the polarising angle. If, however, we include terms of the second order in d_1, then I will be a minimum when $\phi = \alpha - x$, where x is a quantity of the second order in d_1. Using the approximation $f(\phi) = f(\alpha - x) = f(\alpha) - xf'(\alpha)$, we get the following equation to determine x—

$$\cdot\left(R - x\frac{dR}{d\phi}\right)\left(\frac{dR}{d\phi} - x\frac{d^2R}{d\phi^2}\right) + \left(\rho - x\frac{d\rho}{d\phi}\right)\left(\frac{d\rho}{d\phi} - x\frac{d^2\rho}{d\phi^2}\right) = 0,$$

in which ϕ is to be put equal to α after differentiating.

Since $R = 0$ when $\phi = \alpha$, this gives

$$x = \rho\frac{d\rho}{d\phi}\bigg/\left(\frac{dR}{d\phi}\right)^2 \text{ radians,}$$

i.e., $$x = \frac{\mu^3 d_1^2}{2(\mu^2 + 1)(\mu^4 - 1)^2}[1 + \mu^2 - F - E\mu^2]$$

$$\times [(1 + \mu^2)(1 + \mu^4) - F(1 + 4\mu^2 + \mu^4) + E\mu^2(1 + \mu^4)].$$

This is the *diminution* of the polarising angle, and the formula shows that the layer will not always diminish the polarising angle along with the intensity of reflection, but may increase the one and diminish the other.

The values of x (expressed in minutes and seconds) for the nine laws considered above, and the corresponding polarising angle $(\alpha - x)$, are as follows:—

Law ...	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
	° ′ ″	° ′ ″	° ′ ″	° ′ ″	° ′ ″	° ′ ″	° ′ ″	° ′ ″	° ′ ″
x	0 27 38	0 16 24	0 13 30	0 0 0·58	0 31 40	0 10 12	0 19 33	−7 16	0 30 15
$\alpha - x$	56 5 12	56 17 26	56 20 20	56 33 49	56 2 10	56 23 38	56 14 18	56 41 6	56 3 35

The mean of Conroy's estimates of the polarising angle with this particular glass was 56° 23′ 30″. This agrees most closely with the deduction from Law VI, the difference being only 8 seconds. This law was found to fit in best with the experimental measures of the intensity, so that it is probably a close approximation to the truth. The corresponding values of μ' are represented graphically in the continuous curve of fig. 2 below. A similar representation of Law II would show that the values of μ' for these two laws are not very different, and a glance at the tables above makes it evident that Law II would represent the facts almost as well as Law VI.

Fig. 2.
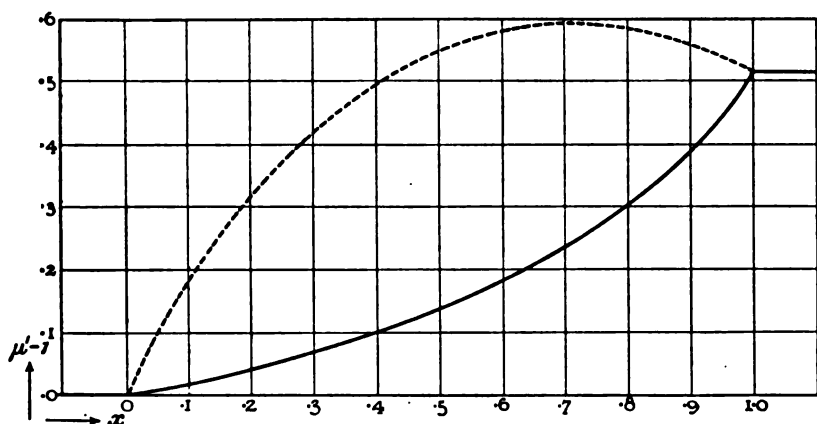
Conroy's experiments on the amount of light transmitted by glass plates of different thicknesses, and under different conditions of polish, agree well with his estimates of the reflecting power. They prove that the departure from Fresnel's law is certainly not due to an irregular scattering of the light at the surface, as has sometimes been suggested. That this is not the explanation of the apparent discrepancy between theory and experiment is also manifest from the fact that both Rayleigh and Conroy found that freshly polished surfaces reflect *more* than Fresnel's formula indicates. Conroy's experiments, immediately after repolishing, were not so numerous as those previously discussed. The results are consequently not nearly so consistent as before, and we cannot build much upon them as regards the law of variation of the refractive index. It will, perhaps, suffice to take a single law, as an illustration of a possible condition of affairs.

Let $\mu'^2 = 1 + ax - \beta x^2$, $\alpha = \beta + \mu^2 - 1$. Then

$$E = \frac{1}{\mu^2}\int_0^1 \mu'^2\, dx = \frac{1}{\mu^2}\left[\frac{1}{2} + \frac{\beta}{6} + \frac{\mu^2}{2}\right]; \quad H = \frac{1}{\mu^2}\int_0^1 dx \int_0^x \mu'^2 dx = \frac{1}{\mu^2}\left[\frac{1}{3} + \frac{\beta}{12} + \frac{\mu^2}{6}\right]$$

$$\frac{a}{\mu^3 d_1^2} = E^2\mu^2 + 1 - 2E - 2H\,(\mu^2 - 1) = \frac{1}{36\mu^2}[\beta^2 - 3 - 3\mu^2\,(\mu^2 - 2)];$$

so that $$\beta^2 = 3 + 3\mu^2\,(\mu^2 - 2) + 36 a d_1^{-2}.$$

In order to increase the reflective power, we must have a positive, and this requires β to be greater than $\{3+3\mu^2(\mu^2-2)\}^{\frac{1}{2}}$, or, in the present case, $\beta > 2\cdot24$.

By way of trial we shall take $\beta = 3$, and we then get

$$E = 0\cdot9358; \quad H = 0\cdot4209; \quad F = 1\cdot132; \quad L-J = 0\cdot2210.$$

Taking the correction to the intensity at normal incidence to be $0\cdot0022$, the following are the values for the various constants :—$a = 0\cdot022$ $b = -0\cdot0434; \quad c = 0\cdot0170; \quad d_1 = 0\cdot3625.$

The *diminution* of the polarising angle, calculated from the formula of p. 26, is $1'\,5''$, so that the polarising angle is $56°\,32'\,45''$, which agrees exactly with the mean of Conroy's measurements. The experimental estimates of the intensity were most consistent at incidences of $10°$, $30°$, $50°$, $61°$, and $75°$. The following table sets out the results and compares them with those obtained from theory with the constants given above :—

$\phi =$	10°.	30°.	50°.	65°.	75°.
Theory	0·0441	0·0455	0·0617	0·1248	0·2571
Experiment	0·0441	0·0455	0·0627	0·1228	0·2633
Difference	0	0	−0·0010	+0·0020	−0·0062

The results are also represented graphically in fig. 3 below.

FIG. 3.
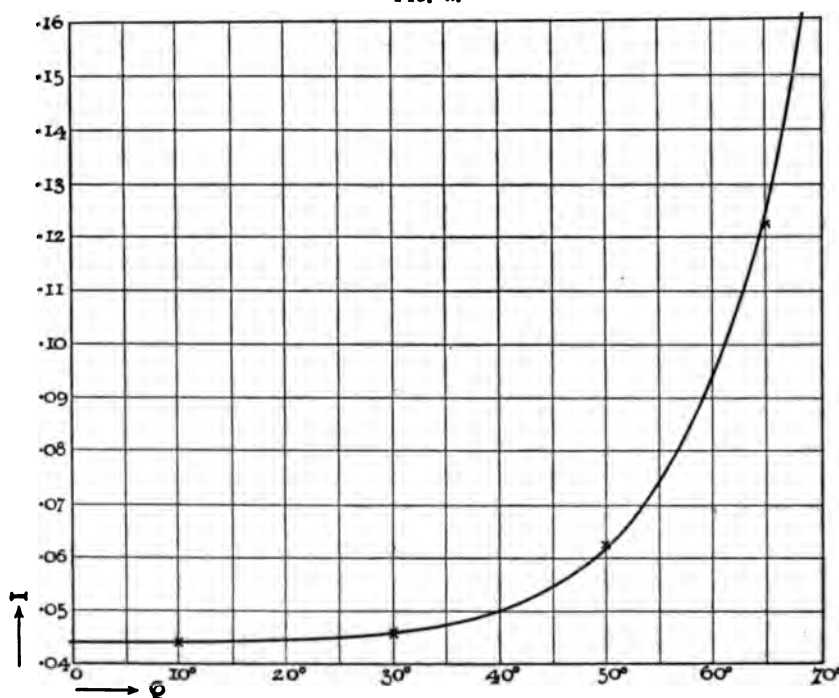
Considering the uncertainty of the experimental results, the agreement is as close as could be expected. The dotted curve in fig. 2 above represents the march of μ' within the layer.

So far we have dealt solely with the influence of a perfectly transparent layer on the intensity of reflection and the position of the polarising angle. We have verified that such a layer, whether uniform or continuously varying, has no effect, if it is so thin that squares and higher powers of d_1 can be neglected. This need not be the case if the layer were of absorbing material, and it may be worth while to consider briefly what would be the effect of a such a layer.

At normal incidence, when $\phi = 0$, we have, with our previous notation,

$$r = \frac{(\mu-1)+id_1\mu(E\mu-1)}{(\mu+1)+id_1\mu(E\mu+1)}$$

$$= \frac{\mu-1}{\mu+1}\left[1+\frac{i2\mu^2 d_1}{\mu^2-1}(E-1)\right] \begin{array}{l}\text{(neglecting squares and}\\ \text{higher powers of } d_1) \end{array}$$

$$= R(1+\alpha e^{i\beta}).$$

Thus the amplitude of the reflected wave is increased by multiplying by the factor $1+\alpha\cos\beta$.

In the layer, let $\mu' = Me^{-i\gamma}$, then we have

$$E = \frac{1}{\mu^2}\int_0^1 M^2\cos 2\gamma \, dx - \frac{i}{\mu^2}\int_0^1 M^2\sin 2\gamma \, dx = A - iB, \text{ say.}$$

And $\alpha\cos\beta$ is the real part of $i(E-1).2\mu^2 d_1/(\mu^2-1)$, and is therefore equal to $2B\mu^2 d_1/(\mu^2-1)$.

If the layer were transparent throughout we should have $\gamma = 0$ and therefore $B = 0$, so that, to this order, as we have seen, there would be no change of intensity. For an absorbing medium, however, γ will not be zero, but will be less than $\frac{1}{2}\pi$, so that $\sin 2\gamma$ will necessarily be positive and B consequently positive. Thus the effect of such a layer will be to increase the reflecting power. The observed departure from Fresnel's formula for a freshly polished surface might, then, be caused by a very thin layer of absorbing material, due either to the polishing powder or to contamination with some foreign substance of a greasy nature. Rayleigh* showed that the deviation of the ellipticity from Fresnel's formula in the neighbourhood of the polarising angle was due to greasy contamination. In a later paper† he followed out the same idea when dealing with the light reflected from water at nearly perpendicular incidence. The reflection actually observed, even after the surface was cleaned, was about $1\frac{1}{2}$ per cent.

* 'Phil. Mag.,' 1892 ; 'Scientific Papers,' vol. 3, p. 496.
† 'Phil. Mag.,' 1892 ; 'Scientific Papers,' vol. 4, p. 3.

greater than that given by Fresnel's formula. "The disagreement is too small a foundation upon which to build with any confidence," but from what we have seen a very slight residual contamination might help to bridge the slight difference between theory and observation.

If we are dealing with incidences other than normal, we have to distinguish between vibrations parallel and perpendicular to the plane of incidence. In both cases we have equations of the form $r = R(1 + \kappa)$, where κ is a small quantity of the first order in d_1. The increase of the intensity due to the layer is $\kappa_1 R_1{}^2 + \kappa_2 R_2{}^2$. Here κ_1 is the real part of

$$id_1 \left[\frac{E\mu^2 \cos\phi\cos\phi' - \mu + \sin^2\phi \cdot F\mu^{-1}}{\mu\cos\phi - \cos\phi'} - \frac{E\mu^2\cos\phi\cos\phi' + \mu - \sin^2\phi \cdot F\mu^{-1}}{\mu\cos\phi + \cos\phi'} \right]$$

$$= \frac{2id_1 \cos\phi}{\mu^2\cos^2\phi - \cos^2\phi'} [\mu^2(E-1) + (F-E)\sin^2\phi].$$

Similarly, κ_2 is the real part of

$$\frac{2id_1 \cos\phi \cdot \mu^2(E-1)}{\mu^2\cos^2\phi' - \cos^2\phi}.$$

The increase of the intensity is therefore

$$\kappa\cos\phi \left[\frac{\mu\cos\phi - \cos\phi'}{(\mu\cos\phi + \cos\phi')^3}(1 - e\sin^2\phi) + \frac{\mu\cos\phi' - \cos\phi}{(\mu\cos\phi' + \cos\phi)^3} \right],$$

where κ and e are constants depending on the thickness of the layer and the law of the distribution of μ' within it. As a numerical illustration we may choose κ and e, so as to give the same results as those found for the transparent layer immediately after repolish. The consequent intensities and their comparison with Conroy's observations are set out in the table below :—

$\phi =$	10°.	30°.	50°.	65°.	75°.
Theory	0·0441	0·0457	0·0622	0·1248	0·2562
Experiment	0·0441	0·0455	0·0627	0·1228	0·2633
Difference	0	+0·0002	−0·0005	+0·0020	−0·0071

The differences between the results for the absorbing and for the transparent layer are not sufficiently marked to enable us to decide definitely between the two hypotheses merely on the ground of the reflective power. To settle such a matter conclusively we should require much more accurate experimental results than are now at our disposal.

The Electric or Magnetic Polarisation of a Thin Cylinder of Finite Length by a Uniform Field of Force.

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§ 1. *Introduction.*

The problem to be considered is the calculation of the polarisation induced in a cylindrical rod of finite length by a uniform field of force parallel to its axis.

The only formula previously given appears to be that of Green* for the normal component of the polarity at the surface of the rod. In the following investigation the method of solution of the general problem of induction by series is used, and expressions are given in §§ 4 and 5 for the mean moment of the rod and the induction across the central section. It is assumed that the susceptibility of the rod is independent of the applied force; consequently the formulæ apply especially to a dielectric rod suspended in a uniform field of electric force, this being, in fact, the purpose for which the calculations were made.

In the case   ong thin rods in a magnetic field it has been assumed that the demagnetising factor might be taken as that of an ellipsoid inscribable in the rod; but this neglects the fact of the non-uniformity of the field within the rod, and various experimental investigations have shown that the simple hypothesis is untenable. In § 7 these experimental results are discussed in relation to the formulæ obtained in the previous sections.

§ 2. *The Series Solution of the General Problem.*

Consider a body placed in a magnetic field whose potential is V, and let a constant κ denote the magnetic susceptibility of the substance. Let Q be the potential of the induced magnetism and ϕ the total potential; then we have

$$\phi = Q + V.$$

* Green, 'Mathematical Papers,' p. 106; also Maxwell, 'Electricity and Magnetism' vol. 2, § 439.

The components of the intensity of magnetisation I at any point are given by

$$I = -\kappa\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)\phi.$$

If $d\nu$ be the inward-drawn normal at the surface of the body, the problem to be solved in finding Q may be expressed in the equation

$$Q = \kappa\int \frac{\partial(V+Q)}{\partial\nu}\frac{d\sigma}{r}, \tag{1}$$

where the integral extends over the surface of the body.

The exact solution of this problem can only be found in a limited number of cases, as, for example, when the surface of the body is an ellipsoid. A method of approximating to a solution was given by Beer,[*] and has been further developed by Neumann,[†] Riecke,[‡] and Wassmuth.[§] The method may be regarded physically as one of successive superpositions in the manner of Murphy.[||] Suppose, as a first approximation, that the potential V produces an induction I_1 equal to $-\kappa(\partial/\partial x, \partial/\partial y, \partial/\partial z)V$; then the distribution I_1 will have a potential V_1, which may in its turn be supposed to induce a distribution I_2, and so on. The total induction will be given by the sum of the series I; and the success of the method depends upon the convergency of this series.

Defining a series of functions by the relations

$$V_1 = \int\frac{\partial V}{\partial\nu}\frac{ds}{r}; \qquad V_2 = \int\frac{\partial V_1}{\partial\nu}\frac{ds}{r}; \text{ and so on,} \tag{2}$$

the first form of series for the induced potential Q, given by Beer, was

$$Q = 4\pi\kappa V_1 + (4\pi\kappa)^2 V_2 + (4\pi\kappa)^3 V_3 + \dots . \tag{3}$$

But even if the intermediary potentials decrease in magnitude, as in most practical cases, this series for Q is convergent only for a limited range of values for κ. Other forms of series have been obtained which include Beer's series, but give a wider range of convergency; two such series given by Riecke and Neumann are equivalent and are expressed in terms of the functions V_1, $V_2 \dots$ by

$$Q = \rho V_1 + \rho^2(V_1+V_2) + \rho^3(V_1+2V_2+V_3) + \dots , \tag{4}$$

where $\qquad\qquad \rho = 4\pi\kappa/(1+4\pi\kappa) = 4\pi\kappa/\mu.$

* Beer, ' Elektricität und Magnetismus,' p. 155.

† C. Neumann, ' Das logarithm. Potential,' p. 248.

‡ Riecke, 'Wied. Ann.,' vol. 13, p. 466, 1881.

§ Wassmuth, ' Wied. Ann.,' vol. 51, p. 367, 1894.

|| Murphy, ' Electricity,' p. 93, 1833.

This series is certainly convergent for all practical cases in which the intermediary potentials form a decreasing series, for instance, in the case of an ellipsoid placed in a uniform field parallel to an axis ;* for then we find

$$V = -Hx; \qquad V_1 = \frac{L}{4\pi}Hx; \qquad V_2 = -\left(\frac{L}{4\pi}\right)^2 Hx; \quad \ldots\ldots;$$

where L is the usual constant associated with an ellipsoid and is less than 4π.

Forming the functions for series (4) we obtain

$$\rho V_1 = \frac{\kappa}{\mu}LHx; \qquad \rho^2(V_1+V_2) = \frac{(4\pi-L)\kappa}{\mu}\frac{\kappa}{\mu}LHx;$$

$$\rho^3(V_1+2V_2+V_3) = \frac{(4\pi-L)^2\kappa^2}{\mu^2}\frac{\kappa}{\mu}LHx, \quad \text{etc.}$$

Hence we have

$$Q = \frac{\kappa}{\mu}LHx\left\{1+\frac{(4\pi-L)\kappa}{\mu}+\frac{(4\pi-L)^2\kappa^2}{\mu^2}+\ldots\right\}.$$

But this series is convergent for all values of κ, and in fact gives the known exact solution

$$Q = \frac{\kappa L}{1+\kappa L}Hx.$$

We shall use, then, the series (4) in the following work, in which we consider the case of a long rod in a uniform field.

§ 3. *Series for a Finite Rod.*

We shall consider the case of a cylindrical rod of length $2l$, with flat circular ends of radius a; we write $l/a = m$.

Suppose the rod placed in a uniform field H parallel to its axis, which we take as the axis of x; then we have

$$V = -Hx. \qquad (5)$$

Our object is to calculate the functions $V_1, V_2, \ldots$ defined in (2).
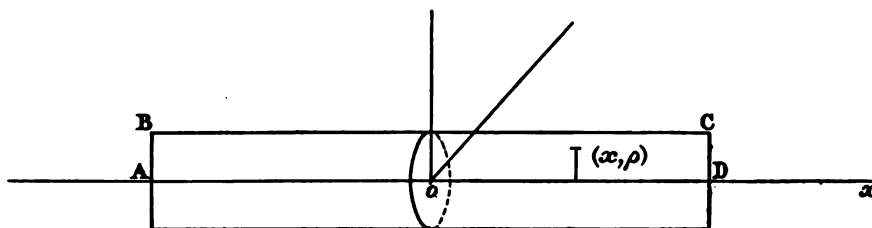
Using cylindrical co-ordinates (x, ρ, θ), we have in general

$$4\pi V_{n+1}(x, \rho) = \int \frac{\partial V_n(x', \rho')}{\partial \nu} \frac{d\sigma}{r} = \int \frac{\partial V_n}{\partial \nu} \frac{d\sigma}{\sqrt{(x'-x)^2 + \rho^2 + \rho'^2 - 2\rho\rho' \cos\theta'}}. \quad (6)$$

Also the element of surface $d\sigma$ is equal to $\rho' ds\, d\theta'$, where ds is equal to dx' or $d\rho'$ according as the point (x', ρ') is on the curved side or a flat end of the rod; and putting

$$R^2 = \rho^2 + \rho'^2 - 2\rho\rho' \cos\theta',$$

we have

$$4\pi V_{n+1}(x, \rho) = \int_0^{2\pi} d\theta' \int \rho' \frac{\partial V_n}{\partial \nu} ds \int_0^\infty e^{\pm\lambda(x'-x)} J_0(\lambda R)\, d\lambda$$

$$= 2\pi \int \rho' \frac{\partial V_n}{\partial \nu} ds \int_0^\infty e^{\pm\lambda(x'-x)} J_0(\lambda\rho) J_0(\lambda\rho')\, d\lambda, \quad (7)$$

where the integral with respect to ds extends over the path ABCD, and the upper or lower sign is taken in the exponential according as $x'-x$ is negative or positive.

Thus we find

$$V_{n+1}(x, \rho) = \tfrac{1}{2} \int_0^a \left(\frac{\partial V_n}{\partial x'}\right)_{x'=-l} \rho' d\rho' \int_0^\infty e^{-\lambda(x+l)} J_0(\lambda\rho) J_0(\lambda\rho')\, d\lambda$$

$$- \tfrac{1}{2} \int_0^a \left(\frac{\partial V_n}{\partial x'}\right)_{x'=l} \rho' d\rho' \int^\infty e^{-\lambda(l-x)} J_0(\lambda\rho) J_0(\lambda\rho')\, d\lambda$$

$$- \tfrac{1}{2} \int_{-l}^x \left(\frac{\partial V_n}{\partial \rho'}\right)_{\rho'=a} a\, dx' \int_0^\infty e^{\lambda(x'-x)} J_0(\lambda\rho) J_0(\lambda a)\, d\lambda$$

$$- \tfrac{1}{2} \int_x^l \left(\frac{\partial V_n}{\partial \rho'}\right)_{\rho'=a} a\, dx' \int_0^\infty e^{-\lambda(x'-x)} J_0(\lambda\rho) J_0(\lambda a)\, d\lambda. \quad (8)$$

From symmetry in the case under consideration, this reduces to

$$V_{n+1}(x, \rho) = -\int_0^a \left(\frac{\partial V_n}{\partial x'}\right)_{x=l} \rho' d\rho' \int_0^\infty e^{-\lambda l} \sinh(\lambda x) J_0(\lambda\rho) J_0(\lambda\rho')\, d\lambda$$

$$- \int_x^l \left(\frac{\partial V_n}{\partial \rho'}\right)_{\rho'=a} a\, dx' \int_0^\infty e^{-\lambda x'} \sinh(\lambda x) J_0(\lambda\rho) J_0(\lambda a)\, d\lambda$$

$$- \int_0^x \left(\frac{\partial V_n}{\partial \rho'}\right)_{\rho'=a} a\, dx' \int_0^\infty e^{-\lambda x} \cosh(\lambda x') J_0(\lambda\rho) J_0(\lambda a)\, d\lambda. \quad (9)$$

Thus at any stage in the evaluation of the successive potentials, V_{n+1} is expressed as the potential of a surface distribution due to V_n; the first integral in (9) gives the part due to the flat ends of the rod and the other two integrals that due to the curved sides.

The potential V_1 can be deduced from (9), or obtained directly as the potential of two uniformly charged circular discs situated at the ends of the rod.

Using the relation

$$\int_0^a \rho' J_0(\lambda\rho')\, d\rho' = a J_1(\lambda a)/\lambda,$$

we obtain

$$V_1 = Ha \int_0^\infty e^{-\lambda l}\sinh(\lambda x)\, J_0(\lambda\rho)\, J_1(\lambda a)\, d\lambda/\lambda. \qquad (10)$$

§ 4. *Calculation of the Total Moment of the Rod.*

The magnetisation at any point of the rod is equal to $-\kappa\,(\partial/\partial x, \partial/\partial y, \partial/\partial z)\,\phi$, where ϕ is the total potential, and the moment of the rod can be calculated by considering the normal component of the polarisation over the surface of the rod. Writing M for the total moment, we have

$$M = -2l\int_0^a 2\pi\kappa\rho\left(\frac{\partial\phi}{\partial x}\right)_{x=l} d\rho - 2\int_0^l 2\pi\kappa a x\left(\frac{\partial\phi}{\partial\rho}\right)_{\rho=a} dx, \qquad (11)$$

where the first integral gives the part due to the ends of the rod, and the second integral that due to the sides.

Now ϕ is given in terms of V and the intermediary potentials V_n according to the series given in (3) and (4); thus from (11) we find that it is required to evaluate expressions of the form

$$U_n = 2l\int_0^a 2\pi\rho\left(\frac{\partial V_n}{\partial x}\right)_{x=l} d\rho + 2\int_0^l 2\pi a x\left(\frac{\partial V_n}{\partial\rho}\right)_{\rho=a} dx. \qquad (12)$$

We shall consider these expressions as far as U_2, and obtain the important terms in their expansions in powers of $1/m$, where m is the ratio of the length of the rod to its diameter, and is assumed to be large.

Then since

$$V = -Hx,$$

we have

$$U = -2\pi a^2 l\kappa H. \qquad (13)$$

Further, from the value of V_1 given in (10) we have

$$U_1 = 4\pi a^2 l H \int_0^\infty e^{-\lambda l}\lambda^{-1}\cosh(\lambda l)\, J_1^2(\lambda a)\, d\lambda$$

$$-4\pi a^2 H \int_0^l x\, dx \int_0^\infty e^{-\lambda l}\sinh(\lambda x)\, J_1^2(\lambda a)\, d\lambda. \qquad (14)$$

If in the second part we perform the integration with respect to x, and put μ for λa, we find that (14) reduces to

$$U_1 = 2\pi a^3 H \int_0^\infty \frac{J_1^2(\mu)}{\mu^2}\, d\mu - 2\pi a^3 H \int_0^\infty e^{-2m\mu}\frac{J_1^2(\mu)}{\mu^2}\, d\mu. \qquad (15)$$

Now we have

$$\int_0^\infty \frac{J_1^2(\mu)}{\mu^2}\, d\mu = \frac{4}{3\pi}.$$

Also, since m is large, the important terms of the second integral are obtained by substituting the value of the Bessel function for small values of the argument; thus as far as the term m^{-2} we have

$$\int_0^\infty e^{-2m\mu} \frac{J_1^2(\mu)}{\mu^2} \, d\mu = \frac{1}{8m} \, . \tag{16}$$

Hence to the same order we have

$$U_1 = 2\pi a^3 H \left(\frac{4}{3\pi} - \frac{1}{8m} \right)$$

$$= 2\pi a^2 l H \left(\frac{4}{3\pi m} - \frac{1}{8m^2} \right). \tag{17}$$

Now we have to evaluate U_2 in a similar manner; we have from the general expression given in (9),

$$\left(\frac{\partial V_2}{\partial x} \right)_{x=l} = - \int_0^a \left(\frac{\partial V_1}{\partial x'} \right)_l \rho' d\rho' \int_0^\infty \lambda e^{-\lambda l} \cosh(\lambda l) J_0(\lambda\rho) J_0(\lambda\rho') \, d\lambda$$

$$+ \int_0^l \left(\frac{\partial V_1}{\partial \rho'} \right)_a a\,dx' \int_0^\infty \lambda e^{-\lambda l} \cosh \lambda x' \, J_0(\lambda\rho) J_0(\lambda a) \, d\lambda$$

$$= - \tfrac{1}{2} \left(\frac{\partial V_1}{\partial x} \right)_l - \tfrac{1}{2} \int_0^a \left(\frac{\partial V_1}{\partial x'} \right)_l \rho' d\rho' \int_0^\infty \lambda e^{-2\lambda l} J_0(\lambda\rho) J_0(\lambda\rho') \, d\lambda$$

$$+ \int_0^l \left(\frac{\partial V_1}{\partial \rho'} \right)_a a\,dx' \int_0^\infty \lambda e^{-\lambda l} \cosh(\lambda x') J_0(\lambda\rho) J_0(\lambda a) \, d\lambda. \tag{18}$$

And, similarly, from (9) we have

$$\left(\frac{\partial V_2}{\partial \rho} \right)_{=a} = - \tfrac{1}{2} \left(\frac{\partial V_1}{\partial \rho} \right)_a + \int_0^a \left(\frac{\partial V_1}{\partial x'} \right)_l \rho' d\rho' \int_0^\infty \lambda e^{-\lambda l} \sinh(\lambda x) J_1(\lambda a) J_0(\lambda\rho') \, d\lambda. \tag{19}$$

It may be noted that if the intermediary potentials V_n be regarded as due to successive surface distributions σ_n, then the equations (18) and (19) are examples of general relations between consecutive surface densities.

Using the values of (18) and (19), we have

$$U_2 = -l \int_0^a 2\pi\rho \left(\frac{\partial V_1}{\partial x} \right)_l d\rho - l \int_0^a 2\pi\rho d\rho \int_0^a \left(\frac{\partial V_1}{\partial x'} \right)_l \rho' d\rho' \int_0^\infty \lambda e^{-2\lambda l} J_0(\lambda\rho) J_0(\lambda\rho') \, d\lambda$$

$$+ 2l \int_0^a 2\pi\rho d\rho \int_0^l \left(\frac{\partial V_1}{\partial \rho'} \right)_a a\,dx' \int_0^\infty \lambda e^{-\lambda l} \cosh(\lambda x') J_0(\lambda\rho) J_0(\lambda a) \, d\lambda$$

$$- \int_0^l 2\pi a x \left(\frac{\partial V_1}{\partial \rho} \right)_a dx + 2 \int_0^l 2\pi a x\,dx \int_0^a \left(\frac{\partial V_1}{\partial x'} \right)_l \rho' d\rho' \int_0^\infty \lambda e^{-\lambda l} \sinh(\lambda x) J_1(\lambda a)$$

$$J_0(\lambda\rho') \, d\lambda. \tag{20}$$

Using the formulæ

$$\int_0^\infty d\lambda \int_q^p \lambda \rho \phi\,(\rho)\,J_n\,(\lambda\rho)\,J_n\,(\lambda r)\,d\rho = \phi\,(r), \qquad q < r < p,$$

$$\int_0^\infty J_0\,(\lambda\rho)\,J_1\,(\lambda a)\,d\lambda = \frac{1}{a}, \qquad \rho < a,$$

we find that (20) reduces to

$$U_2 = -\int_0^l 2\pi a x \left(\frac{\partial V_1}{\partial\rho}\right)_a dx - 4\pi a \int_0^a \left(\frac{\partial V_1}{\partial x'}\right)_l \rho' d\rho' \int_0^\infty e^{-\lambda l} \sinh\,(\lambda l)\,J_0\,(\lambda\rho')\,J_1\,(\lambda a)\frac{d\lambda}{\lambda}$$

$$+ 4\pi a l \int_0^l \left(\frac{\partial V_1}{\partial\rho'}\right)_a a\,dx' \int_0^\infty e^{-\lambda l}\cosh\,(\lambda x')\,J_0\,(\lambda a)\,J_1\,(\lambda a)\,d\lambda. \qquad (21)$$

We substitute now for V_1 from (10) and write

$$x = a\xi; \quad \rho' = a\eta; \quad l = am; \quad \mu = \lambda a; \quad \mu_1 = \lambda' a.$$

Hence we obtain

$$U_2 = 2\pi H a^3 \int_0^m \xi d\xi \int_0^\infty e^{-m\mu_1}\sinh\,(\mu_1\xi)\,J_1^2\,(\mu_1)\,d\mu_1$$

$$-4\pi H a^3 \int_0^1 \eta d\eta \int_0^\infty e^{-m\mu_1}\cosh\,(m\mu_1)\,J_0\,(\mu\eta)\,J_1\,(\mu_1)\,d\mu_1$$

$$\int_0^\infty e^{-m\mu}\sinh\,(m\mu)\,J_0\,(\mu\eta)\,J_1\,(\mu)\frac{d\mu}{\mu}$$

$$-4\pi H a^2 l \int_0^m d\xi \int_0^\infty e^{-m\mu_1}\sinh\,(\mu_1\xi)\,J_1^2\,(\mu_1)\,d\mu_1$$

$$\int_0^\infty e^{-m\mu}\cosh\,(\mu\xi)\,J_0\,(\mu)\,J_1\,(\mu)\,d\mu. \qquad (22)$$

The first two terms give the following:

$$2\pi H a^3 m \int_0^\infty e^{-m\mu_1}\cosh\,(m\mu_1)\,J_1^2\,(\mu_1)\frac{d\mu_1}{\mu_1} - 4\pi H a^3 \int_0^\infty e^{-m\mu}\sinh\,(m\mu)\,J_1^2\,(\mu)\frac{d\mu}{\mu^2}$$

$$-2\pi H a^3 \int_0^1 \eta d\eta \int_0^\infty e^{-2m\mu_1}J_0\,(\mu_1\eta)\,J_1\,(\mu_1)\,d\mu_1 \int_0^\infty e^{-m\mu}\sinh\,(m\mu)\,J_0\,(\mu\eta)\,J_1\,(\mu)\frac{d\mu}{\mu}.$$

Also, in the third term of (22) we perform the integration with respect to ξ; then in all the terms of U_2 we apply the previous method of approximation, that is, we consider m large and substitute the lower terms of the expansions of the Bessel functions for small values of the argument. Using also the relation

$$\int_0^\infty \frac{J_1^2\,(\mu)}{\mu}\,d\mu = \tfrac{1}{2},$$

and keeping to the order in which the parts of U_2 are given above, the approximation indicated gives, to the order $1/m^3$,

$$U_2 = \pi \mathrm{H} a^2 l \left(\frac{1}{2} + \frac{1}{16m^2} - \frac{8}{3\pi m} + \frac{1}{4m^2} - \frac{1}{6\pi m^3} - \frac{1}{2} + \frac{1}{8\pi m^3} - \frac{1}{16m^2} \right)$$

$$= \pi \mathrm{H} a^2 l \left(-\frac{8}{3\pi m} + \frac{1}{4m^2} - \frac{1}{24\pi m^3} \right). \tag{23}$$

Comparing U_2 with U_1 given in (17), we see that they both begin with a term of the same order $1/m$; but we have

$$U_1 + U_2 = -\frac{1}{24} \pi \mathrm{H} a^2 l \frac{1}{m^3}. \tag{24}$$

Returning now to the series (3) and (4) for the induced potential Q, we see that in calculating the total moment of the rod in this manner it is of advantage to use the series

$$Q = \frac{4\pi\kappa}{\mu} V_1 + \left(\frac{4\pi\kappa}{\mu} \right)^2 (V_1 + V_2) + \ldots, \qquad \mu = 1 + 4\pi\kappa.$$

Then, if we denote by I_m the mean moment per unit volume obtained by calculating the moment of the whole bar, we have from (13), (17), and (24)— as far as the order indicated—

$$I_m = \kappa \mathrm{H} \left\{ 1 - \frac{4\pi\kappa}{\mu} \left(\frac{4}{3\pi m} - \frac{1}{8m^2} \right) + \left(\frac{4\pi\kappa}{\mu} \right)^2 \frac{1}{48m^3} \right\}. \tag{25}$$

§ 5. *The Mean Induction through the Central Section.*

Another quantity which we require to calculate is the mean polarisation over the central transverse section of the bar; if this be denoted by I_c, we have

$$I_c = -\frac{\kappa}{\pi a^2} \int_0^a 2\pi \rho \left(\frac{\partial \phi}{\partial x} \right)_{x=0} d\rho, \tag{26}$$

where $\phi = -\mathrm{H}x + Q.$

To evaluate the contributions made by V_1 and V_2, we have from (10),

$$\frac{1}{\pi a^2} \int_0^a 2\pi \rho \left(\frac{\partial V_1}{\partial x} \right) d\rho = \frac{2\mathrm{H}}{a} \int_0^a \rho \, d\rho \int_0^\infty e^{-\lambda l} J_0(\lambda\rho) J_1(\lambda a) \, d\lambda$$

$$= 2\mathrm{H} \int_0^\infty e^{-m\mu} J_1^2(\mu) \, d\mu/\mu$$

$$= \mathrm{H} \left(\frac{1}{2m^2} - \frac{3}{4m^4} \right), \tag{27}$$

to the order indicated, using previous method of approximation.

From the general expression in (9) we have V_2 given in the form

$$V_2 = -Ha \int_0^a \rho' d\rho' \int_0^\infty e^{-\lambda_1 l} \cosh(\lambda_1 l) J_0(\lambda_1 \rho') J_1(\lambda_1 a) d\lambda_1$$

$$\int_0^\infty e^{-\lambda l} \sinh(\lambda x) J_0(\lambda\rho) J_0(\lambda\rho') d\lambda$$

$$+ Ha^2 \int_x^l dx' \int_0^\infty e^{-\lambda_1 l} \sinh(\lambda_1 x') J_1{}^2(\lambda_1 a) d\lambda_1$$

$$\int_0^\infty e^{-\lambda x'} \sinh(\lambda x) J_0(\lambda\rho) J_0(\lambda a) d\lambda$$

$$+ Ha^2 \int_0^x dx' \int_0^\infty e^{-\lambda_1 l} \sinh(\lambda_1 x') J_1{}^2(\lambda_1 a) d\lambda_1$$

$$\int_0^\infty e^{-\lambda x'} \cosh(\lambda x') J_0(\lambda\rho) J_0(\lambda a) d\lambda \quad (28)$$

Hence we have

$$\left(\frac{\partial V_2}{\partial x}\right)_{x=0} = -Ha \int_0^a \rho' d\rho' \int_0^\infty e^{-\lambda_1 l} \cosh(\lambda_1 l) J_0(\lambda_1 \rho') J_1(\lambda_1 a) d\lambda_1$$

$$\int_0^\infty \lambda e^{-\lambda l} J_0(\lambda\rho) J_0(\lambda\rho') d\lambda$$

$$+ Ha^2 \int_0^l dx' \int_0^\infty e^{-\lambda_1 l} \sinh(\lambda_1 x') J_1{}^2(\lambda_1 a) d\lambda_1$$

$$\int_0^\infty \lambda e^{-\lambda x'} J_0(\lambda\rho) J_0(\lambda a) d\lambda. \quad (29)$$

The mean value of this taken over the circle $x = 0$, $\rho = a$, is given by

$$\frac{1}{\pi a^2} \int_0^a 2\pi\rho \left(\frac{\partial V_2}{\partial x}\right)_0 d\rho$$

$$= -2H \int_0^a \rho' d\rho' \int_0^\infty e^{-\lambda_1 l} \cosh(\lambda_1 l) J_0(\lambda_1 \rho') J_1(\lambda_1 a) d\lambda_1 \int_0^\infty e^{-\lambda l} J_1(\lambda a) J_0(\lambda\rho') d\lambda$$

$$+ 2Ha \int_0^l dx' \int_0^\infty e^{-\lambda_1 l} \sinh(\lambda_1 x') J_1{}^2(\lambda_1 a) d\lambda_1 \int_0^\infty e^{-\lambda x'} J_0(\lambda a) J_1(\lambda a) d\lambda \quad (30)$$

We proceed to evaluate these integrals for m large by substituting the expansions of the Bessel functions as before; then the first integral in (30) becomes, to the required order,

$$-\frac{H}{a^2} \int_0^a \rho' \left\{1 + \frac{1}{8m^2} - \frac{3}{16}\left(\frac{\rho'^2}{4a^2} + \frac{1}{8}\right)\frac{1}{m^4}\right\} \left\{\frac{1}{2m^2} - 3\left(\frac{\rho'^2}{4a^2} + \frac{1}{8}\right)\frac{1}{m^4}\right\} d\rho'$$

$$= -H\left(\frac{1}{4m^2} - \frac{13}{32}\frac{1}{m^4}\right). \quad (31)$$

The second integral in (30) is equivalent to

$$H \int_0^\infty \int_0^\infty \left\{\frac{e^{-m\mu}}{\mu_1 - \mu} + \frac{e^{-m(\mu + 2\mu_1)}}{\mu_1 + \mu} - \frac{e^{-m\mu_1}}{\mu_1 - \mu} - \frac{e^{-m\mu_1}}{\mu_1 + \mu}\right\} J_1{}^2(\mu_1) J_0(\mu) J_1(\mu) d\mu \, d\mu_1.$$

Substituting values of the Bessel functions of μ or μ_1, or of both, according to the exponential term, this reduces to

$$H\left(\frac{1}{4m^2}-\frac{35}{32}\frac{1}{m^4}\right). \tag{32}$$

Adding this to the part given in (31), we see that the mean value of $\partial V_2/\partial x$ over the central section begins with a term $-23H/32m^4$, while the mean value of $\partial V_1/\partial x$ begins with a term of the order $1/m^2$.

Then, substituting in (26) the values calculated above, we have, as far as the order shown,

$$I_c = \kappa H-\kappa\left\{4\pi\kappa H\left(\frac{1}{2m^2}-\frac{3}{4m^4}\right)-(4\pi\kappa)^2 H\frac{23}{32m^4}\right\}$$

$$= \kappa H\left\{1-\frac{2\pi\kappa}{m^2}+\pi\kappa\left(3+\frac{23}{2}\pi\kappa\right)\frac{1}{m^4}\right\}. \tag{33}$$

§ 6. *Application to Dielectric Polarisation.*

If an ellipsoid of specific inductive capacity K is placed in a uniform electric field, it is known that the field within the ellipsoid is uniform, and the polarisation at any point is given by a formula

$$I = \kappa\,(H-NI); \qquad \kappa = (K-1)/4\pi. \tag{34}$$

The factor N is a numerical factor independent of I, and can be calculated theoretically; for a prolate spheroid, of which m is the ratio of the longer to the shorter axis, we have

$$N = \frac{4\pi}{m^2-1}\left\{\frac{m}{\sqrt{m^2-1}}\log_e(m+\sqrt{m^2-1})-1\right\}, \tag{35}$$

the axis of revolution being along the direction of the field. Also, for an infinite rod of circular section, N is zero for a uniform field parallel to the axis of the cylinder, and is equal to 2π for a field at right angles to the axis.

In the case of a rod of finite length placed in a uniform field, there is no longer uniformity of the field within the rod, but as we suppose the specific inductive capacity to be independent of the field, we have still an equation of the form (34). For a field parallel to the axis of the rod, we have from (25) to the first order of $1/m$, the ratio of diameter to length,

$$N = 16/3Km. \tag{36}$$

For a field at right angles to the axis we may still take N to be equal to 2π. Now, in determinations of the specific inductive capacity of a dielectric in the form of a cylindrical rod, it is necessary to measure the couple

required to keep the rod at a given angle ϕ to the direction of the external field. If we put V for the volume of the rod and use the values of N obtained above, we have

$$\text{Couple on rod} = \kappa^2 \text{V} \frac{2\pi - 16/3\text{K}m}{(1+2\pi\kappa)(1+16\kappa/3\text{K}m)} \text{H}^2 \sin\phi \cos\phi, \qquad (37)$$

where
$$\kappa = (\text{K}-1)/4\pi.$$

§ 7. *The Demagnetising Factor of a Finite Rod.*

When the problem is one of magnetic induction, it is clear that the previous results only supply an approximation to a solution; for, since the field is not uniform within the rod, it follows that the magnetic permeability μ varies along the rod, thus complicating the problem to be solved. In fact, the demagnetising force will not be expressible in the form NI, where N is a numerical factor independent of I.

On the supposition that there is such a constant N, at least approximately, for long thin rods, Du Bois[*] made a comparison between the values of N for ovoids and cylindrical rods of the same dimension-ratio m; the factors for the rods were calculated from experiments by Ewing for the longer rods and by Tanakadaté for the shorter ones.

It was pointed out by Mann[†] that in the former experiments ballistic methods were used, but in the latter magnetometric methods. Consequently the quantities measured were those denoted by I_m and I_c above; and the factor N deduced by the two methods will, in general, be different, and may be denoted by N_m and N_b, being the magnetometric and ballistic values of the demagnetisation factor. From the series given in (25) and (33) we have, for large values of m, the approximate values

$$\text{N}_m = \frac{16}{3\mu m}; \qquad \text{N}_b = \frac{2\pi}{m^2}. \qquad (38)$$

Benedicks[‡] further investigated the values of N_m and N_b for rods and, in particular, their variation with the intensity of magnetisation; the value of the demagnetising force $N_b I$ at the centre of the rod was found to increase with the field, and then after a certain point to decrease rapidly.

Using the ballistic method, Lamb[§] determined the induction through sections taken at intervals along a bar, and was thus able to trace curves

[*] Du Bois, ' Annalen der Physik,' vol. 46, p. 495, 1892.
[†] C. R. Mann, 'Physical Review,' vol. 3, p. 359, 1895.
[‡] Benedicks, 'Annalen der Physik,' vol. 6, p. 726, 1901.
[§] C. G. Lamb, 'Phil. Mag.,' vol. 48, p. 262, 1899.

showing the distribution of induction and force along the bar and the consequent effective distribution of magnetic permeability.

Searle and Bedford* investigated the demagnetising force h at the centre of a long cylindrical rod. Determining the values of h for increasing values of the external force H, they found that h increases at first more rapidly than $2\pi I_c/m^2$, but after passing a maximum it descends to a minimum somewhat less than that value; the latter result is interpreted as being due to hysteresis effects.

A quantity measured in several experiments was the ratio I_m/I_c, giving the effective length of the bar.

Using expressions (25) and (33) above, we have approximately

$$I_m/I_c = 1 - \left(\frac{4\pi\kappa}{\mu}\right)\frac{4}{3\pi m}.$$

With a rod for which m was 25, Benedicks found this ratio increased to 0·84 at the highest value of H used in the experiment.

Reviewing the experimental results, it appears that in the case of magnetic induction the facts of the non-uniformity of the force within the rod and the consequent variation of effective susceptibility are too important to be neglected; hence, in this case, the calculations of the previous sections supply limiting values towards which the quantities approach as the magnetisation tends to saturation.

* Searle and Bedford, 'Phil. Trans.,' A, vol. 198, p. 98, 1902.

The Velocity of the Negative Ions in Flames.

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The following paper contains an account of a series of experiments on the electrical conductivity of a coal-gas flame, the principal object being to determine the velocities of the negative ions in the flame produced either by the ionisation of salt-vapours or by the ionisation of the flame gases. Two methods have been used, and the results arrived at are concordant.

The first method depends on a determination of the ratio between the potential gradient in the flame at some distance from the electrodes and the current flowing through it. This method was used to determine the velocity of the ions of the flame gases.

. The second method depends on finding the potential gradient necessary to cause the negative ions due to salt-vapour to move across the flame from one electrode to the other while carried upwards with the stream of gas.

The results obtained show that the velocity of negative ions in the flame due to a potential gradient of 1 volt per centimetre is about 10,000 cm. per second. The calculated velocity for a negative electron or corpuscle is about 13,000 cm. per second, so that it appears that the negative ions in flames are probably electrons.

Previous determinations of the velocity of the negative ions of various salt-vapours in flames have been made by several other observers, and all agree in finding the velocity to be about 1000 cm. per second only. It is shown that this discrepancy is due to the assumption made by the previous experimenters that, for small potential differences, the potential gradient between the electrodes is uniform. The experiments to be described show that this is very far from being the case, even when the potential difference between the electrodes is a fraction of a volt.

A discussion of the results previously obtained is contained in a recent paper by H. A. Wilson.* J. J. Thomson† has calculated the velocity of an ion in a flame, and has suggested that the negative ions in flames are electrons initially, but afterwards get loaded with electrically-neutral

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* "The Velocities of the Ions of Alkali Salt Vapours at High Temperatures," 'Phil. Mag.,' June, 1906.

† "Conduction of Electricity through Gases," p. 204.

molecules. This view has also been put forward as possible by H. A. Wilson and by Lenard.

The results obtained in the present paper show conclusively that the negative ions are electrons and not atoms.

Direct Conductivity Measurements.

The apparatus for the first series of experiments consisted of the quartz-tube burner previously described by H. A. Wilson.* The tube was 25 cm. long and 2 cm. in diameter, and had a row of 40 holes, each 1·5 mm. in diameter, uniformly distributed along a line parallel to the axis of the tube.

FIG. 1.

T_1T, tube burner.	V, voltmeter.
F F, flame.	G, galvanometer.
E E, electrodes.	K, key.
P P, glass tubes.	C, commutator.
D D, fine platinum wires.	Q, quadrant electrometer.
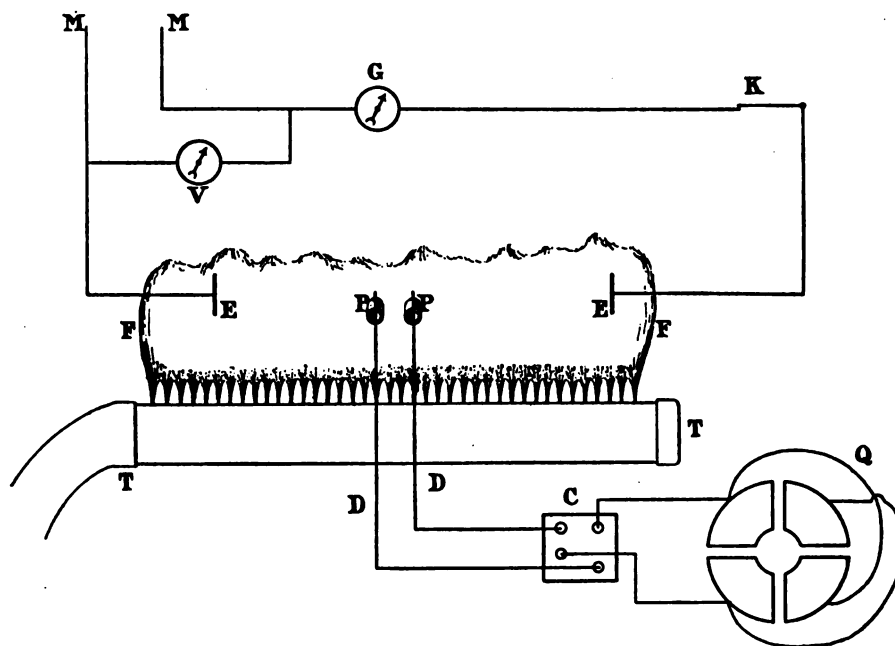
M M, wires leading to source of E.M.F.

The gas and air from a large Bunsen burner were admitted to this tube and burnt at the holes. In this way a long, fairly uniform, flame was obtained and, as the quartz insulates well, there was no fear of conduction down the flame and along the tube.

* 'Phil. Mag.' June, 1905, p. 476.

The electrodes used consisted of a pair of circular platinum discs 1·6 cm. in diameter. They were supported in the flame so that they were clear of the green cones, and they could be adjusted to any desired position. Fig. 1 is a diagram of the apparatus.

In most of the experiments one electrode was kept fixed near one end of the flame while the other was moved horizontally along the flame. The current through the flame was measured by a moving-coil galvanometer and the potential difference between the electrodes by an electrostatic voltmeter. The potential gradient in the flame was measured by means of two fine platinum wires immersed in the flame and connected to the quadrants of a Thomson's electrometer. H. A. Wilson[*] has stated that for large distances between the electrodes the effect of putting salt on the negative electrode appears to be to increase the conductivity of the flame.

Experiments were made to test this effect, and for currents from $7·3 \times 10^{-6}$ to 261×10^{-6} ampère it was found not to exist.[†]

Potential difference between principal electrodes.	Current i, unit is 10^{-5} amp.	Distance between principal electrodes.	Distance between wires.	Potential gradient X.	X/i.	Remarks. Disc electrodes.
volts.		cm.	cm.	volts cm.		
106	0·73	16·4	0·8	0·4	0·55	No salt, slight deposit
106	0·52	16·4	0·8	0·32	0·61	No salt
106	2·64	16·4	0·8	1·55	0·59	NaCl on cathode
106	3·95	16·4	0·8	2·50	0·63	NaCl ,,
106	4·15	16·4	0·8	3·02	0·72	KCl ,,
106	6·07	16·4	0·8	4·58	0·75	KCl ,,
106	7·58	16·4	0·8	5·70	0·75	K_2CO_3 ,,
106	9·00	9·0	0·8	6·68	0·74	K_2CO_3 ,,
106	11·6	9·0	0·8	7·78	0·67	K_2CO_3 ,,
106	4·08	9·0	0·8	3·05	0·74	NaCl ,,
208	3·67	17·0	0·5	2·52	0·69	Slight deposit
208	6·81	17·0	0·5	4·18	0·61	K_2CO_3 on cathode
208	9·82	17·0	0·5	5·80	0·59	K_2CO_3 ,,
208	11·8	9·0	0·5	9·32	0·79	K_2CO_3 ,,
208	14·7	7·0	0·5	10·54	0·72	K_2CO_3 ,,
208	18·5	5·5	0·5	12·42	0·67	K_2CO_3 ,,
208	22·2	4·5	0·5	15·2	0·68	K_2CO_3 ,,
208	23·6	4·5	0·5	17·3	0·73	K_2CO_3 ,,
208	26·1	4·5	0·5	18·8	0·72	K_2CO_3 ,,
16·5	3·5	9·0	1·1	2·76	0·79	K_2CO_3 ,,
16·5	1·73	16·0	—	1·27	0·74	K_2CO_3 ,,
16·5	1·02	16·0	1·1	0·86	0·84	K_2CO_3 ,,

The above table gives some of the results obtained. The galvanometer

[*] 'Phil. Mag.,' 1905, p. 476.

[†] A large increase in the conductivity of the flame between the electrodes was obtained ater by putting salt on both electrodes ; see p. 63, *infra.*

had a resistance of 220 ohms, and gave a deflection of one scale division for a current 11.5×10^{-9} ampère. The electrometer gave a deflection of one scale division for a potential difference of 0·023 volt, the deflection in all cases being a double one.

In the table the different values of the current, obtained with the same E.M.F. and salt and distance between the electrodes, are due to changes in the position of the salt-bead in the flame just below the negative electrode.

The mean value of X/i deduced from this set is 0·70 in the units used. The diameter of the electrodes was 1·6 cm., so that the ratio of the potential gradient to the current per square centimetre is approximately $0.7 \times \pi \times 0.8 \times 0.8 = 1.40$, which in C.G.S. units is $1.40 \times 10^8 \times 10^6$ or 1.40×10^{14}.

The conductivity of the flame is therefore 7.2×10^{-15} C.G.S. unit.

This conductivity has been obtained on the assumption that the current flowed uniformly through a cylinder from electrode to electrode. This is not the case, since the current will spread out and flow through the whole of the flame. In the experiments the flame was not quite so wide as the electrodes, but a conducting part extended above and below the electrodes. These parts were, however, colder than the part where the gradient was measured, and the assumption that the coolness of the edges of the flame and these conducting portions which project beyond the cylinder compensate for each other cannot be far from the truth.

We can from this determine approximately the velocity of the ions; for if e is the charge on an ion and n the number of ions per cubic centimetre, then the current density is given by the formula—

$$i = Xen\,(k_1 + k_2),$$

where $X =$ potential gradient,

$(k_1, k_2) =$ velocities of positive and negative ions respectively due to unit potential gradient.

Thus the conductivity of the flame is

$$ne\,(k_1 + k_2) = 7.2 \times 10^{-15}.$$

Now ne may be estimated roughly from the results obtained by Professor Wilson and the writer.[*] It is shown in the paper referred to that the number of ions per cubic centimetre in a flame is given by $ne = V_0 k^2/2\pi D^2$, where, in the experiments described, $V_0 = 1.2$ electrostatic units of potential, $D = 0.6$ cm., and K is the " apparent specific inductive capacity " of the flame

* "On the Electrical Conductivity of Flames containing Salt Vapours for Rapidly Alternating Currents," 'Phil. Mag.,' April, 1906.

gases for rapidly alternating currents. For the flame without salt K was found then to be approximately 2.

Another value of K can be got by comparing the results obtained with alternating currents and those previously obtained with steady currents.* It is shown in the paper referred to above that $K = 6.66\sqrt{k'} + 1$, where k' is the steady current due to an E.M.F. of 0·227 volt. For the free flame this was 0·052 in the units used, so that $K = 6.66\sqrt{0.052} + 1 = 2.5$.

Taking K to be the mean of these two values, we get

$$ne = \frac{1.2 \times (2.3)^2}{2\pi \times (0.6)^2} = 2.81 \text{ electrostatic units,}$$

$$= 9.4 \times 10^{-11} \text{ electromagnetic unit.}$$

Therefore we may write

$$9.4 \times 10^{-11}(k_1 + k_2) = 7.2 \times 10^{-15},$$

or $k_1 + k_2 = 8 \times 10^{-5}$ nearly,

which gives a value 8000 under 1 volt per centimetre.

Now k_1, the velocity of the positive ions, is only about 60 cm./sec., so that we get $k_2 = 8000$ cm./sec. approximately. Owing to the uncertainty about the value of K, this result can only be regarded as a rough approximation.

Conduction Balanced against Convection.

The second series of experiments was undertaken in order to obtain the velocity of the negative ions by finding the minimum electric force necessary to drive some of them from one electrode to the other, assuming that the ions had an upward velocity equal to that of the flame gases. This method was used by H. A. Wilson† and G. Moreau,‡ the velocity being deduced from the observations on the assumption of a uniform potential gradient across the flame. The present investigation includes measurements of this gradient for applied E.M.F.'s of the same magnitude as those necessary to drive the ions across the flame.

The following is the arrangement adopted: Gas and air were led into a jar fitted with a cork through which three equal glass tubes passed; the mixture issuing from these tubes was burnt at three equal small copper cylinders fitting thin glass tubes, placed vertically over the tubes fitting the jar and joined to them by short pieces of wide rubber-tubing. The flames so obtained were in every way similar and burned very steadily,

* Smithells, Dawson, and Wilson, ' Phil. Trans.,' A, 1900, p. 89.
† 'Phil. Trans.,' A, 1899, p. 499.
‡ 'Annales de Chimie et de Physique,' 1903.

the height of the green cones remaining constant throughout the experiments.

The flame tubes passed through three holes in a wooden stand, which served also to support tubes carrying the electrodes. These were plane platinum rectangles 4·7 cm. long and 2·1 cm. wide; they were made rigid by thick platinum wires welded diagonally across them. The flame and the electrodes were surrounded by a metal cylinder which shielded the flame from draughts. The electrodes were connected through the galvanometer to a potentiometer.

Fig. 2 is a diagram of the apparatus. To obtain the minimum potential gradient necessary to drive some of the ions across the flame, the current-E.M.F. curves were obtained for the free flame and for the flame with salt vaporised beneath the negative electrode, with various distances between the electrodes.

FIG. 2.

F F F, flames.   M M, metal shield.
E E, electrodes.   W W, wooden stand.
A A, glass tubes. T, thermo-couple.
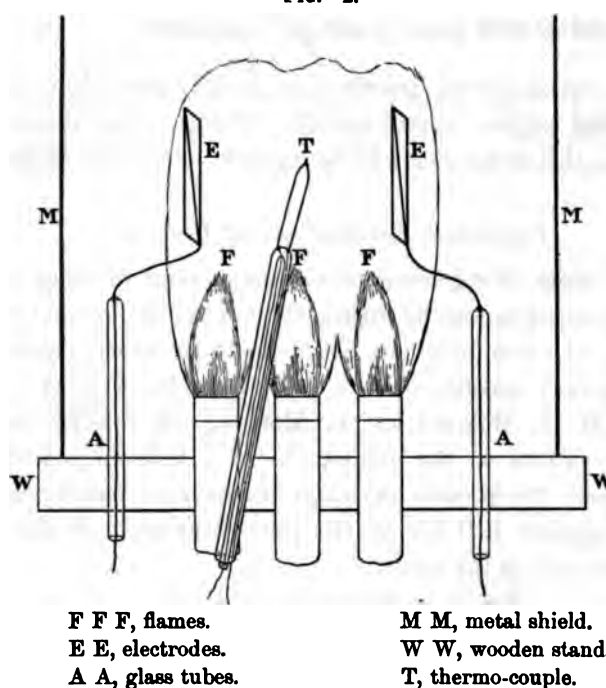
Figs. 3 and 4 give two pairs of such curves for distances 3·1 and 3·7 cm.

The curve for the free flame is very nearly a straight line. When the salt bead is put in the flame beneath the negative electrode, the curve still remains nearly straight and in the same direction for small E.M.F.'s, but it gradually curves upwards until at a certain stage the rise has become

Electrodes 3·1 cm. apart.

Fig. 3.

Electrodes 3·7 cm. apart, 4·7 cm. long.
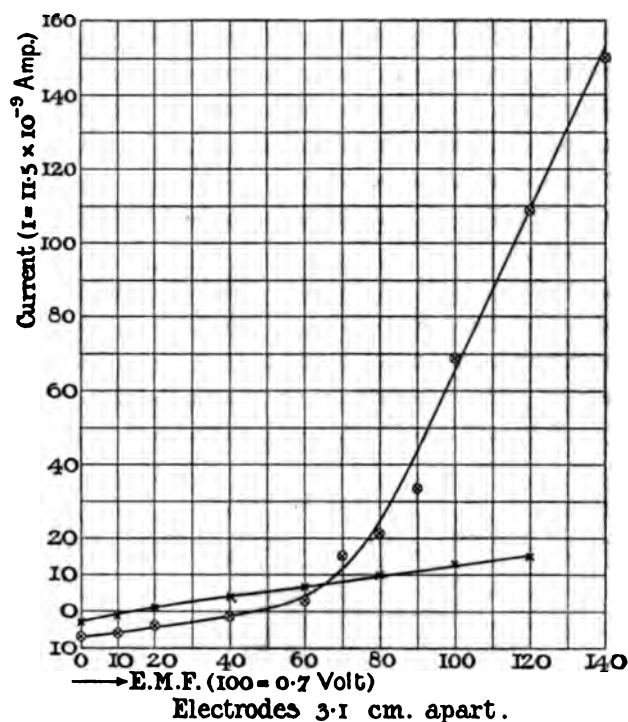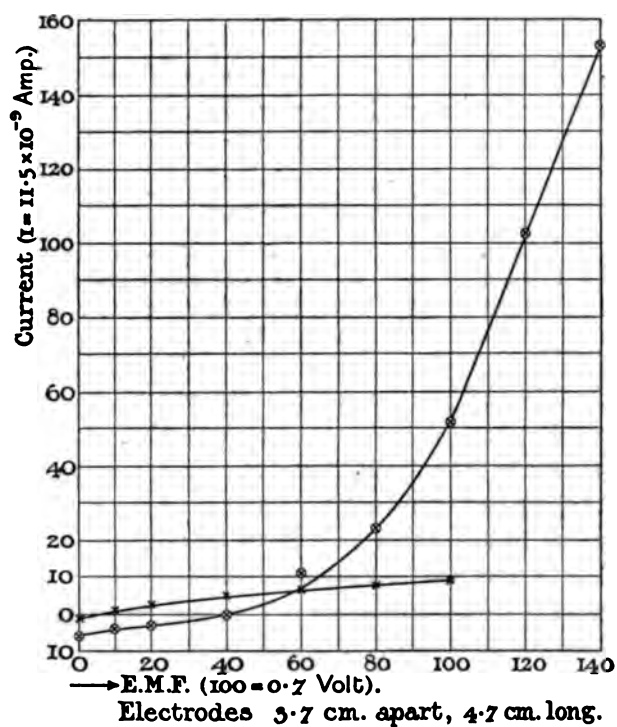
much more rapid, and the curve is again approximately a straight line, but has a much greater inclination. It is assumed that this latter stage is reached when the E.M.F. applied becomes just enough to carry some of the rising ions entirely across the flame, from the bottom of the negative to the top of the positive electrode.

In the curves given the critical stage is reached for E.M.F.'s of 0·5 and 0·56 volt respectively.

The variation in the potential taken up by a platinum wire in the Bunsen flame depended on at least four things: (1) temperature changes in the flame, including changes in ionisation due to temperature alone; (2) changes in ionisation arising from vaporisation of salt in the flame; (3) changes in the E.M.F. applied to the electrodes; (4) changes in position relative to the electrodes.

Fig. 5.

B, battery.   G₁ G₂, galvanometers.
P P, potentiometer.   Q, quadrant electrometer.
V, voltmeter.   Pt Rh, thermo-couple wires.
          W, water bath.
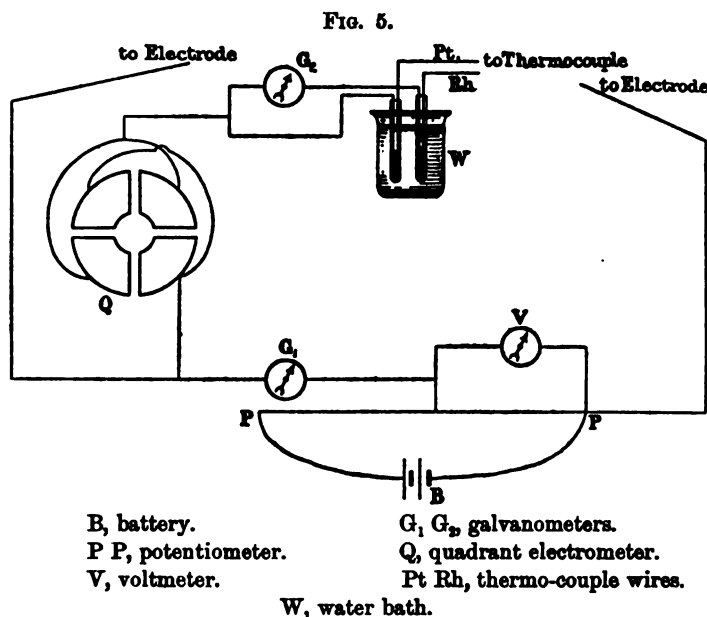
The object in this part of the experiments was to determine that part of the effect of (4) which was due to applied E.M.F. alone, and as it was impossible to eliminate (1) and (2), it was necessary to determine separately the effect due to these and to correct for it.

For this purpose it was decided to use a thermo-couple as explorer, the couple consisting of two fine platinum and platinum-rhodium wires twisted together, the twisted part being about 1 mm. long, and the wires then bent back at right angles so that the distance between the parallel parts was about 6 mm.

The thermo-couple was supported on the stand belonging to a reading microscope, and could be adjusted, by sliding along the graduated stand, to any position in the flame.   The supporting tube passed through a rectangular window in the metal shield, and to keep the flame as steady and free from draughts as possible, the tube carried a metal shutter which closed up the window while enabling the couple to be moved across the flame.

The thermo-couple was standardised by finding the galvanometer deflection when a small bead of K_2SO_4 was just melted at the junction.   The temperature corresponding to this was taken to be 1066° C., and that corresponding to any other deflection was calculated by first finding the "platinum temperature" and then reducing to the Centigrade scale by the curve given by Callendar.*

At first an attempt was made to find how the potential taken up by the thermo-couple depended on its temperature; it was found that, when there was no applied E.M.F., the couple was always at a potential higher than that of the electrodes, and that the potential difference between them varied approximately as the difference of temperature.

Fig. 6 shows the variation of temperature as the exploring couple moved from electrode to electrode.

FIG. 6.
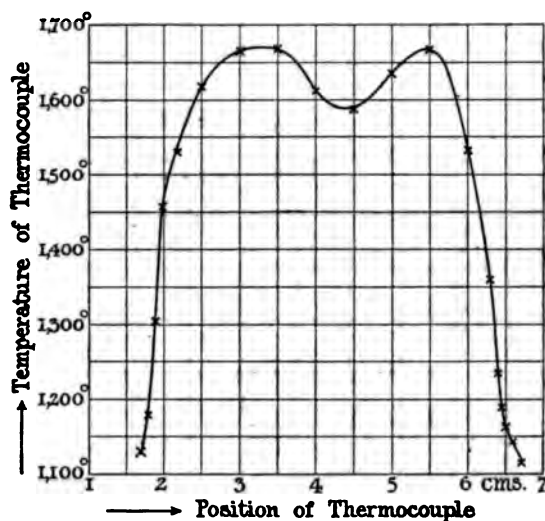
Fig. 7 shows the way the potential difference between the couple and the electrodes changes as the couple is moved, there being no applied E.M.F.

* 'Phil. Mag.,' vol. 48, 1899, p. 533.

and no salt, and the electrodes being connected together, so as to be at one
potential.

Fig. 8 shows the corresponding variation when K_2CO_3 is vaporised beneath
the electrode (B).

FIGS. 7 and 8.
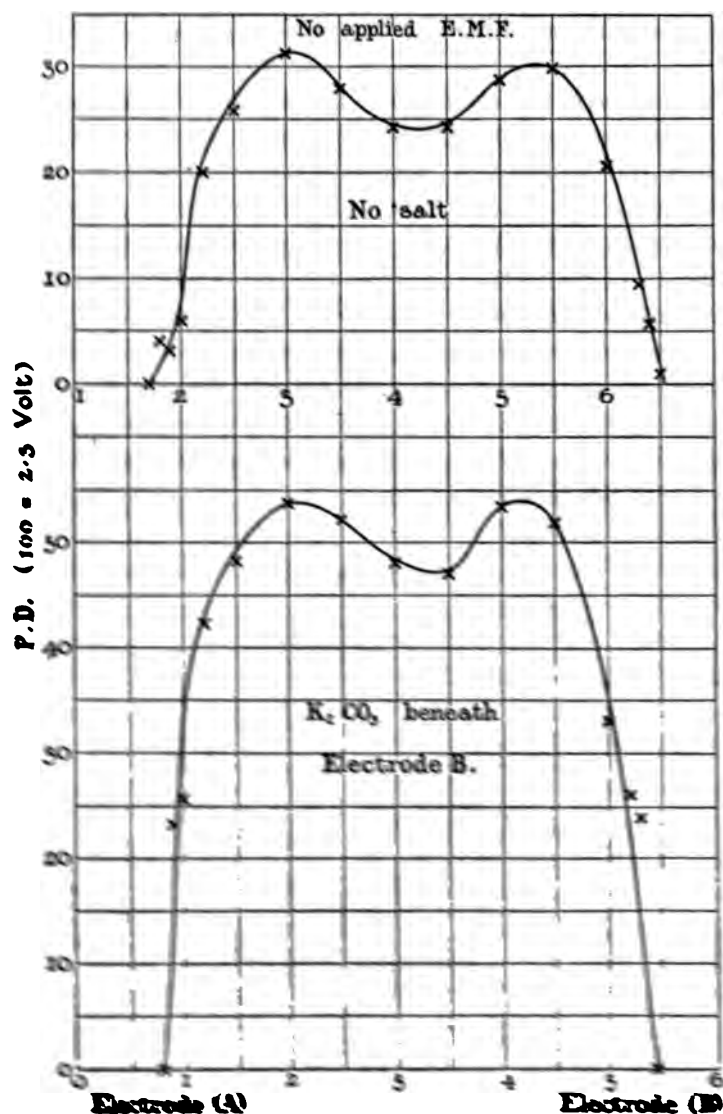
It will be seen that the Curves 7 and 8 are very similar, with gradients
the same on the right and left sides, but that the maximum potential
difference in 8 is nearly double what it is in 7. Thus, putting salt on one

electrode makes the difference of potential between the thermo-couple and the electrodes greater than before. In each case electric equilibrium cannot supervene until ions have accumulated at the electrodes.

From these results corrections were applied to the values obtained for the gradient with an applied E.M.F., and from the results deduced in this way it was seen that the major part of the fall still took place at the electrodes, at the negative electrode for the free flame, and at the positive electrode when salt is vaporised beneath the cathode.

It was not possible, however, to obtain in this way accurate results for the gradient in the body of the flame. The assumption was, therefore, made that when the temperature, registered by the thermo-couple at a particular point in the flame, was unchanged and the vaporisation of salt at the electrodes remained steady, the change in the potential, taken up by the thermo-couple when a potential difference was applied to the electrodes, represented accurately the change in the potential due to the applied potential difference. The temperature at a point in the flame oscillates about a mean value, and it is assumed that when the temperature at a particular point has this mean value, the temperatures at other points are also mean-value temperatures. To obtain results, with this condition holding, the following method was adopted :—

The thermo-couple was set at a certain height and moved across the flames from one electrode to the other in steps of a millimetre near the electrodes and 0·5 cm. in the middle of the flame. For every different position of the thermo-couple the galvanometer and electrometer readings were taken (1) with the electrodes connected and no E.M.F. applied; (2) with applied E.M.F.'s of 0·35, 0·7, and 1·4 volts. These readings were all taken without any change in the condition of the flame or in the position of the thermo-couple or electrodes.

The difference between the electrometer deflections (for a given position of the thermo-couple) with no applied E.M.F. and with an applied E.M.F. was taken as the true potential difference between the point in the flame and the electrodes due to the E.M.F. applied. In this way the true fall of potential across the flame, due to the applied E.M.F.'s, was found, errors due to the thermo-couple not taking up the potential of the flame being eliminated.

The temperature of the thermo-couple in any given position was not quite constant, owing to draughts which it was found impossible entirely to prevent. Thus the time-temperature curve of the thermo-couple in a given position in the flame is a continuous curve with maxima and minima oscillating about a mean value ; the electrometer readings for this position

were all taken when the thermo-couple indicated this mean value of the temperature.

The following tables give some of the readings taken in this way.

In Column I are the deflexions of the thermo-couple galvanometer; in II the current through the flame; III gives the distance in centimetres of the couple from the anode; IV, the deflections of the electrometer; V, the potential difference applied to principal electrodes in volts.

April 4th.—Curve 12. No salt. Thermo-couple 2 cm. below top of electrodes. Distance between electrodes, 5 cm.

I.	II.	III.	IV.	V.	I.	II.	III.	IV.	V.
147	4	0	0	0	239	8	3·3	29	0
	14	—	58	1·38		16	—	81·5	1·38
157	4	0·1	4	0	244	8	3·8	30	0
	14	—	55	1·38		17	—	80	1·38
179	5	0·2	3·5	0	219	8	4·3	20·5	0
	15	—	54	1·38		17	—	71·5	1·38
206	5	0·3	6	0	189	9	4·6	9·5	0
	15	—	58	1·38		18	—	59	1·38
219	5	0·5	20	0	167	9	4·7	5·5	0
	16	—	72	1·38		18	—	54·5	1·38
236	6	0·8	26	0	159	9	4·75	5	0
	16	—	78	1·38		18	—	52·5	1·38
244	6	1·3	32	0	153	9	4·8	1	0
	16	—	84·5	1·38		18	—	13	1·38
244	6	1·8	28	0	149	10	4·9	1	0
	16	—	80·5	1·38		19	—	8·5	1·38
234	7	2·3	24·5	0	146	10	5·0	0	0
	16	—	75·5	1·38		19	—	0	1·38
230	8	2·8	24	0					
	17	—	77	1·38					

April 5th.—K₂CO₃ beneath B. Thermo-couple 0·7 cm. below top of electrodes. 2·1 volts on potentiometer. Distance between electrodes, 4·8 cm.

I.	II.	III.	IV.	V.	I.	II.	III.	IV.	V.
129	− 20	0	0	0	230	− 24	2·4	48	0
	+ 688	—	60	1·38		− 5	—	48·5	0·35
	+ 88	—	31	0·7		88	—	48·5	0·7
	+ 3	—	15·5	0·35		488	—	55·5	1·38
143	− 20	0·1	27	0	237	− 19	2·9	51	0
	688	—	50	1·38		0	—	51	0·35
	98	—	35	0·7		88	—	53	0·7
	− 2	—	30	0·35		538	—	57	
160	− 20	0·2	36	0	236	− 18	3·4	53·5	0
	− 2	—	31	0·35		0	—	53·5	0·35
	98	—	38	0·7		88	—	55	0·7
	648	—	49	1·38		588	—	58	1·38
196	− 22	0·4	42	0	220	− 22	3·9	43	0
	− 4	—	45	0·35		0	—	43	0·35
	88	—	46·5	0·7		88	—	42	0·7
	688	—	56	1·38		688	—	45	1·38
229	− 22	0·9	50	0	180	648	4·4	15	1·38
	− 5	—	51·5	0·35		− 22	—	11	0
	98	—	52·5	0·7		0	—	11·5	0·35
	648	—	60	1·38		88	—	12	0·7
240	− 24	1·4	50·5	0	129	− 22	4·6	−10	0
	− 6	—	51·5	0·35		648	—	− 6	1·38
	98	—	51·5	0·7		0	—	−10	0·35
	648	—	59	1·38		88	—	−11	0·7
285	− 25	1·9	48·5	0	118	− 22	4·75	0	0
	− 6	—	48·5	0·35		638	—	0	1·38
	78	—	51	0·7		88	—	0	0·7
	648	—	56	1·38		0	—	0	0·35

April 10th.—K$_2$CO$_3$ beneath B. Thermo-couple 2·7 cm. beneath top of electrodes. 2·1 volts on potentiometer. Distance between electrodes, 4·6 cm.

I.	II.	III.	IV.	V.	I.	II.	III.	IV.	V.
144	− 14	0	0	0	223	− 32	2·7	47	0
	12	—	15·5	0·35		10	—	49	0·35
	110	—	29·5	0·7		220	—	50·5	0·7
	520	—	60	1·38				53·5	1·38
158	− 13	0·1	23·5	0	238	− 35	3·2	53·5	0
	10	—	25	0·35		15	—	54·5	0·35
	120	—	30	0·7		220	—	55·5	0·7
	620	—	44	1·38				57	1·38
178	− 20	0·2	26	0	228	− 38	3·7	51·5	0
	5	—	29	0·35		20	—	52	0·35
	130	—	31	0·7		200	—	54	0·7
	720	—	45	1·38				57	1·38
218	− 25	0·4	42·5	0	206	− 30	4·2	33	0
	4	—	44	0·35		12	—	33	0·35
	160	—	47·5	0·7		200	—	33·5	0·7
	820	—	57	1·38				35	1·38
228	− 30	0·7	48	0	188	− 24	4·4	26	0
	5	—	49·5	0·35		20	—	27	0·35
	160	—	51·5	0·7		180	—	27	0·7
	920	—	59·5	1·38				31	1·38
246	− 30	1·2	53·5	0	170	− 25	4·5	24	0
	12	—	54	0·35		12	—	24	0·35
	180	—	55·5	0·7		180	—	25	0·7
	over 900	—	63·5	1·38				26	1·38
248	− 30	1·7	52	0	149	− 25	4·6	0	0
	10	—	52·5	0·35		10	—	0	0·35
	300	—	54	0·7		180	—	0	0·7
			60·5	1·38				0	1·38
226	− 30	2·2	46	0					
	10	—	46·5	0·35					
	210	—	50	0·7					
		—	55·5	1·38					

The current with an applied E.M.F. of 1·38 volts here reached a value too large to be read off on the scale. The mean current for this E.M.F. has been taken to correspond to a reading −700.

Figs. 9, 10, 11 are the curves obtained by plotting the results given in these tables.

It will be seen that the fall of potential consists of a large drop at the electrodes, and of a nearly uniform gradient in the body of the flame.

Fig. 9 gives the gradient for the free flame, and the fall is seen to be mainly at the cathode.
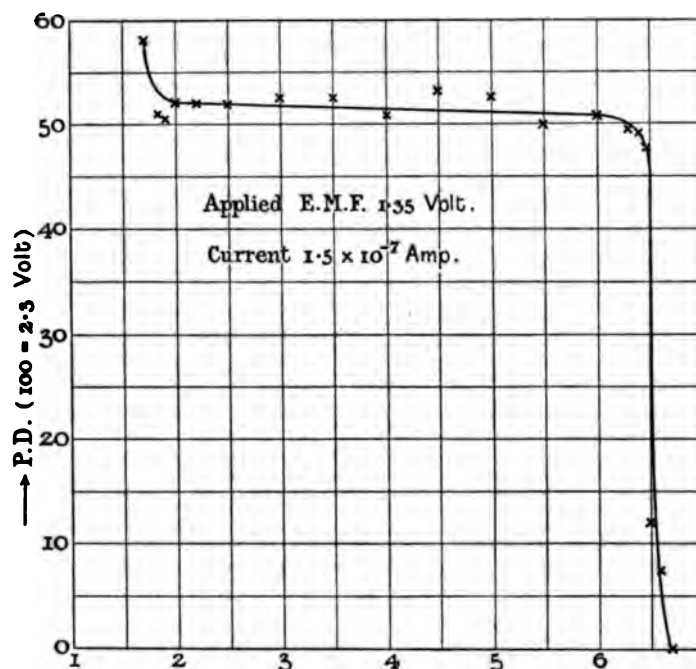
FIG. 9.

Figs. 10, 11 give the fall of potential with salt on the cathode taken along horizontal lines from electrode to electrode at distances 0·7 and 2·7 cm. below the top of the electrodes. The curves are similar, so that the potential gradient does not change appreciably as we move up in the flame so long as we take points within the space included between the electrodes.

The fall of potential is now mainly at the anode, and the fraction of the total fall which occurs there increases as the E.M.F. applied diminishes, while the cathode fall disappears.

The following table gives the results obtained for the potential gradient with an applied potential difference of 1·38 volts :—

Potential difference in volts between electrodes.	Current i $1 = 10^{-5}$ ampère.	Potential gradient X in volts per cm.	Distance of thermo-couple from top of electrodes.	X/i.	Remarks.
			cm.		
1·38	0·73	0·05	0·7	0·068	K_2CO_3 on cathode.
1·38	0·98	0·061	2·0	0·062	,, ,,
1·38	1·1	0·06	2·7	0·055	,, ,,

It is not possible from the readings taken to estimate accurately the potential gradient for the smaller applied E.M.F.'s. We can see, however, that the gradient is very small and that there is no change in the nature of the curve.

Fig. 10.
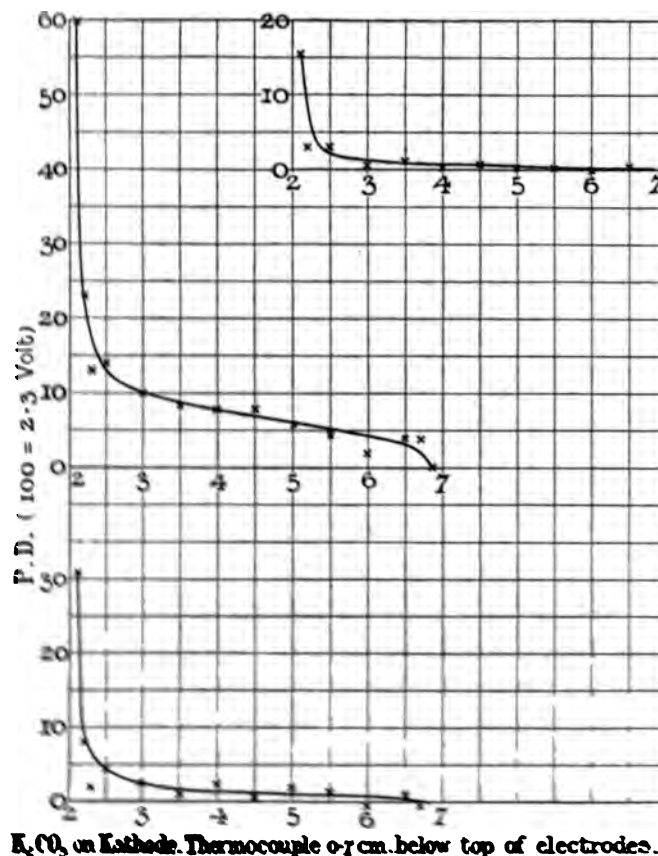
K_2CO_3 on Kathode. Thermocouple 0·7 cm. below top of electrodes.

Now, in the first part of the paper it was proved that the ratio of the current to the potential gradient in the body of the flame was independent of the applied E.M.F. and of the vaporisation of salt on the electrodes. In the present case we find from the experiments the potential gradient for an applied potential difference of 1·38 volts, and, knowing the values of the current for the other applied potential differences, we can deduce the gradient corresponding to them.

Taking the mean value of X/i to be 0·062 from the above table, the following are the gradients deduced in this way for an applied E.M.F. of 0·7 and 0·35 volt :—

Potential difference in volts between electrodes.	Current i $1 - 10^{-5}$ ampère.	Potential gradient X in volts per cm.	Remarks.
0·7	0·13	0·0081	K_2CO_3 on cathode.
0·35	0·02	0·0012	,, ,,
0·7	0·2	0·012	,, ,,
0·35	0·03	0·0018	,, ,,
0·7	0·14	0·0087	,, ,,

Fig. 11.

K_2CO_3 on Kathode. Thermocouple 2·7 cm. below top of electrodes.
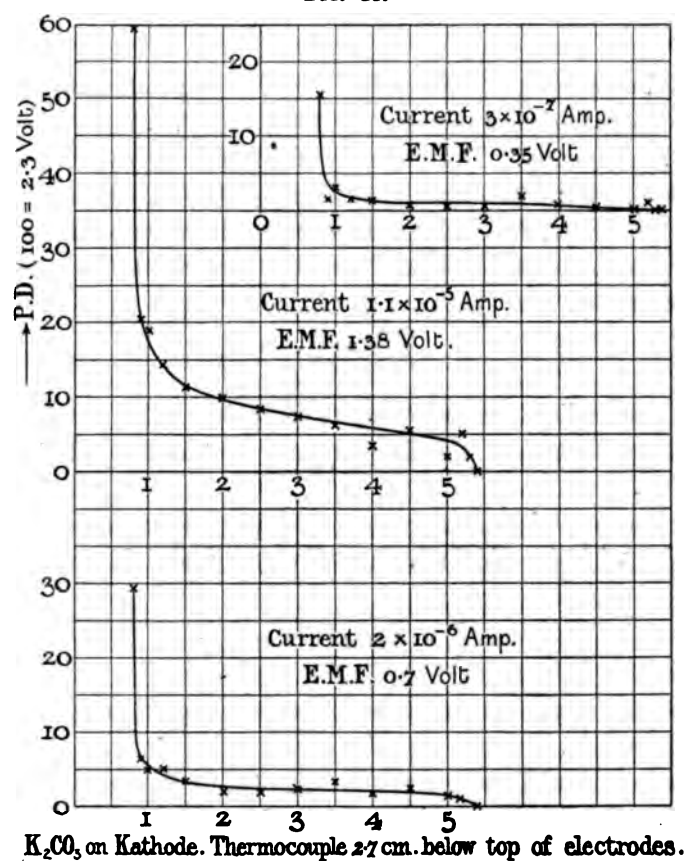
The currents for a given applied potential difference were not quite constant during an experiment, but the ratios were nearly so, and corresponding currents have been taken throughout.

The mean gradient for an applied E.M.F. of 0·7 volt with K_2CO_3 on the negative electrode is 0·0096 volt per centimetre.

The conductivity of the flame deduced from the mean value is i/AX, which is

$$(0\cdot062 \times 10^6 \times 10^8 \times A)^{-1}$$

in C.G.S. units, where A is the area of the cross-section of the conducting part of the flame. The area A cannot be found accurately, but for the flame used, which was about 12 cm. high above the green cones and 2·5 cm. wide, it is estimated that A would be 20 sq. cm., allowance being made for the coolness of the edges and upper parts of the flame.

This gives for the conductivity in C.G.S. units 8×10^{-15} nearly, a result not differing much from the value found for the quartz-tube flame in the earlier experiments.

The E.M.F. at which the current-E.M.F. curve begins to rise rapidly with salt on the negative electrode for a distance between the electrodes of 4·6 cm. is 0·7 volt nearly. Thus, if h is the height of the electrodes, v the upward velocity of the flame gases and therefore of the ions, d the distance between the electrodes, and x the distance the salt vapour extends from the negative electrode, then the velocity k_2 of the negative ions for unit potential gradient is given by

$$\frac{k_2 X}{d-x} = \frac{v}{h},$$

where X is the gradient corresponding to an applied E.M.F. of 0·7 volt, each side being the reciprocal of the time required for the first salt ions just to cross the flame.

Now, the flame containing the vapour extended 1·5 cm. from the electrode to its junction with the middle flame, and we may take this to be the value of x. Hence

$$k_2 = \frac{v}{X} = 69v \times 10^{-8} \text{ nearly,}$$

since $X = 0\cdot0096$ volt per centimetre, or for a gradient of 1 volt per centimetre, $k_2 = 69\,v$.

To determine v, the following method, suggested by Professor H. A. Wilson, was adopted. A plane mirror was attached to one of the prongs of an electrically-driven tuning-fork. The reflection of the flame in this mirror was viewed through a telescope. The reflected images of the paths of bright particles moving up in the flame were approximately sine curves when the mirror was vibrating. If t is the periodic time of the fork, λ the wave-length of the curves seen, v the velocity of the particles upwards, then it is easy to see that $\lambda = vt$. The particles moved very quickly across the field of view and, although the curves could be plainly seen, it was not possible to

accurately measure the wave-length. The paths of the particles were therefore photographed. Lycopodium dust was fed in with the gas and air and was found to give out enough light. The photographs were taken with a camera kindly lent by Mr. H. S. Allen, some on ordinary rapid plates and some on isochromatic plates; the latter give the better results. The negatives show a number of intersecting curves, which it is not easy to disentangle, but occasionally one shows up more distinctly than the rest and can be traced through two or three waves.

A millimetre scale occupying the same position as the flame was also photographed after reflection at the mirror, and this enabled the actual wave-lengths to be obtained. The photographed scale gave 36 divisions for 1 cm. The measurement of the curves gives them a wave-length in the photographs of 0·52 cm., or an actual wave-length of 1·87 cm. The fork used gave 100 complete vibrations per second. Hence the velocity of the particles is 187 cm. per second, or $u = 187$ cm. per second.

Now, the velocity k_2 of the negative ions was found to be $69v$ for a gradient of 1 volt per centimetre, thus

$$k_2 = 69 \times 187 = 12,900 \text{ cm. per second nearly.}$$

The rough estimate obtained in the previous section agrees with this result as well as could have been expected.

The velocity of corpuscles in an electric field may be calculated on the assumption that the corpuscles after impact with molecules act on the whole as though the velocity gained owing to the electric field vanished at impact. This will at least furnish us with a lower limit to the velocity.

Let λ be the mean free path of a corpuscle among the gas molecules, and let u be its mean velocity of agitation. Then the number of impacts in unit time is u/λ, and we may assume that during this time the corpuscle traverses paths of all lengths. The number of these paths whose lengths lie between l and $l + dl$ is

$$\frac{u}{\lambda} \frac{1}{\lambda} \epsilon^{-l/\lambda} dl.$$

The time of describing this path is l/u if we neglect the change due to the velocity added by the electric field. In our case this is permissible, provided the field does not exceed 10 volts per centimetre and we neglect changes produced in paths longer than 100 times the mean free path.

The distance moved in the direction of the field during this time due to the acceleration produced by the field is $\frac{1}{2} \frac{Xe}{m} \frac{l^2}{u^2}$, where X is the intensity

of the field and e and m the charge and mass of a corpuscle. Therefore adding all the paths described in unit time the distance moved will be

$$\frac{1}{2}\int_0^\infty \frac{Xe}{m}\frac{l^2}{u^3}\frac{u}{\lambda^2}e^{-l/\lambda}\,dl = \frac{Xe\lambda^*}{mu}.$$

This will be the mean velocity of the corpuscle due to the field, and k, its velocity in unit field, will be $\lambda e/mu$.

Now $e/m = 10^7$ very nearly.

Townsend[†] has shown experimentally that the mean free path of corpuscles in air is about four times the mean free path of air-molecules at the same pressure and temperature. Taking the temperature of the flame to be $1800°$ C., and the mean free path of a molecule in air to be 10^{-5} cm. at ordinary temperatures, this gives for the mean free path of a corpuscle in the flame

$$\lambda = 4 \times 10^{-5} \times \tfrac{2073}{273} = 3 \times 10^{-4} \text{ nearly.}$$

To get u we assume that the equation $mu^2 = m_1 u_1^2$ holds between the corpuscles and the gas. This gives

$$u = \sqrt{2000} \times 184{,}400 \times \sqrt{\tfrac{2073}{273}},$$

taking the velocity of hydrogen molecules to be 1844 metres per second and the mass of a corpuscle to be $1/1000$ of the mass of an hydrogen atom. Hence

$$u = 2\cdot32 \times 10^7.$$

Therefore, substituting, we get for the velocity of a corpuscle under unit electric field,

$$\frac{3 \times 10^{-4}}{2\cdot32 \times 10^7} 10^7 = 13{,}000 \times 10^{-8},$$

or for 1 volt per centimetre the velocity is 13,000 centimetres per second. This velocity is very approximately the same as that found experimentally above.

It appears, therefore, that the negative ions in the hot parts of flames are free electrons and not atoms.

Determinations of the velocity of the negative ions have previously been made by H. A. Wilson,[‡] by G. Moreau,[§] and by E. Marx.[||] These writers all agree in obtaining for the negative ions a velocity of about 1000 cm. per second for a gradient of 1 volt per centimetre. The results obtained in this paper are of another order, and the difference is probably capable of being explained in the following way. Wilson and Moreau both assumed

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* See Langevin, 'Thèses,' Paris, 1902, p. 47.
† 'Phil. Mag.,' 1901, p. 198; 'Phil. Mag.,' 1903, p. 598.
‡ 'Phil. Trans.,' A, 1899, p. 517.
§ 'Annales de Chimie et de Physique,' 1903, p. 30.
|| 'Annalen der Physik,' vol. 2, 1900, p. 790.

in their determination that the potential fall for small E.M.F.'s consisted wholly of a uniform gradient right across the flame, and that the electrode fall was negligible. The present investigation shows that this is not the case and that the greater part of the fall of potential occurs near the electrodes. The values of the potential gradient in the flame are thus less than they would be if the fall were uniform all across; the previously deduced velocity would therefore be too small.

Marx measured the potential gradient at the electrodes and deduced the velocity on the assumption of uniform ionisation. Near the electrodes the gradient is very large and changes rapidly; thus it is probable that measurements near the electrodes do not give accurately the gradient at the electrodes required by his theory. The measurements of the gradient would be likely to give a value too small and, in consequence, a velocity also too small.

The velocities obtained in the present series of experiments have been only those of vapour of potassium carbonate and of the flame gases. As previous experimenters have shown that the negative ions of all salts have the same velocity, their relative results remain true, although the absolute numbers are subject to correction. It may therefore be concluded that the carriers of the electricity in salt-vapours in flames are corpuscles and are not atoms nor corpuscles loaded with neutral molecules.

A series of measurements were made with salt vaporised beneath both electrodes. In this case the current is very much increased, and the fall of potential consists of nearly equal sudden falls at the electrodes and an approximately uniform gradient in the body of the flame.

Fig. 12 gives the curves obtained from these measurements. It appears from these curves that there are inversions of the gradient near each electrode. These are probably due to the excess of positive ions near the cathode and of negative ions near the anode,* and an inspection of the curves shows that the effect extends for about ¼ cm. from each electrode. We may then conclude that there is a marked excess of ions of one sign in a layer extending 0·5 cm. from each electrode.

The following table gives the results deduced from these observations:—

Distance between electrodes.	Potential difference between electrodes in volts.	Current i $1 = 10^{-5}$ ampère.	Potential gradient X in volts per cm.	X/i.
cm. 4·7	1·38	10	0·16	0·016
4·7	0·7	4	0·073	0·018

* The equation of the potential, $d^2V/dx^2 = -4\pi\rho$, shows that the volume density of electricity is nearly proportional to the curvature, being positive where the curve is concave upwards.

FIG. 12.

K$_2$ CO$_3$ beneath both Electrodes.
Thermocouple 2·7 cm. below top of Electrodes.
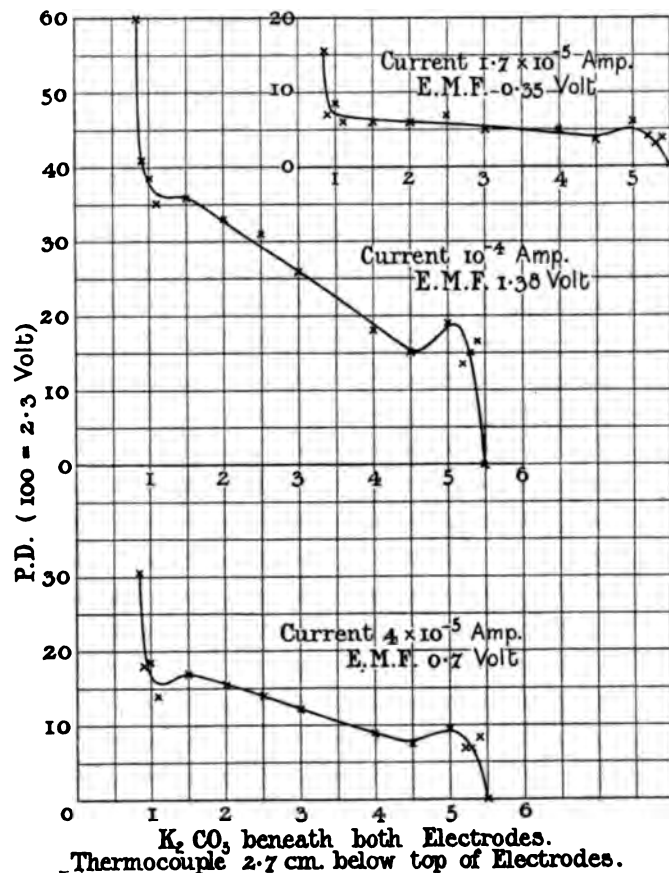
It will be seen from this that the conductivity is greater than in the preceding experiments, although it is practically the same for 1·4 volts as for 0·7 volt. This effect cannot be due to diffusion of the ions; for if such were the case we should expect a conductivity changing from the electrodes towards the centre of the flame, but the curves show that there is no change for a distance of 3 cm., the distance of uniform gradient. Neither can it be due to ions driven into the body of the flame by the electric field, for it is unchanged by changing the applied potential difference. Neither can it be be due to ions shot out from the region near the glowing electrodes, for we should then get a similar result with salt on one electrode only, and this we have seen is not the case.

The accumulation of ions at both electrodes when salt is supplied at both of these points to a higher proportion of ions all along the flame as *infra*, which will account for the fact; further experiments with varying distance

between the electrodes and different salts might elucidate the conditions further.*

As previous experimenters have observed, in all the experiments when the temperatures of the electrodes were different, there was a small current when no E.M.F. was applied and the electrodes were connected together.

This effect was increased when salt was put on one of the electrodes.

This current is inappreciable compared with the currents produced with applied E.M.F.'s greater than 1 volt, but for smaller values of the potential difference this inverse current is comparable with the current due to the applied E.M.F. Throughout these experiments the current due to a small applied E.M.F. has been measured, not from the zero of the galvanometer, but from the scale reading when the galvanometer was connected through the flame. The current is therefore larger by an amount equal to the inverse current, and as this varies with the salt and the temperature of the electrodes, it was necessary to determine the "zero" for each experiment.

The explanation of the inverse current seems to be this. At the surface of the glowing platinum a continual interchange of ions is going on, the hot platinum both emitting ions and absorbing them from the flame. Since the electrodes and galvanometer form an insulated system, a steady state must be reached, when on the whole the emission and absorption are balanced. Since, however, their rates will not depend in the same way on the temperature, one electrode will be emitting more than it absorbs, and *vice versâ* for the other. There will thus be a current through the galvanometer from one electrode to the other.

When salt is put on one electrode, the number of ions in the gas there situated will be increased, and the number absorbed by the electrode will also be increased. The potential of the electrode system will therefore rise until it is sufficiently above the potential of the gas for the increased emission due to the electric force to compensate for the increased absorption. The emission will increase at both electrodes, while the increase in the absorption will be at one only. There will, therefore, be an increased current through the galvanometer which is in accordance with observation.

The negative ions will be the main factors in this interchange, on account of their greater velocity in the flame, so that there will be an excess of negative electricity at that electrode which is in contact with the salt-vapour. The current will therefore be through the galvanometer to that electrode, which agrees with the experimental facts.

* A similar effect was obtained by H. A. Wilson (*loc. cit.*) with salt vapour at the negative electrode only.

In conclusion, I wish to record my indebtedness to Professor H. A. Wilson for much kind advice and encouragement given during the course of these experiments.

On a New Iron Carbonyl, and on the Action of Light and of Heat on the Iron Carbonyls.

By Sir James Dewar, M.A., Sc.D., LL.D., F.R.S., Jacksonian Professor in the University of Cambridge, and Humphrey Owen Jones, M.A., D.Sc., Fellow of Clare College, and Jacksonian Demonstrator in the University of Cambridge.

This paper contains an account of the results of the continuation of the experiments on the action of light on the liquid iron carbonyl (iron pentacarbonyl) and the action of heat on the resulting solid compound, diferro-nonacarbonyl, $Fe_2(CO)_9$, which were described in a paper on "The Physical and Chemical Properties of Iron Carbonyl," communicated to the Society in 1905.[*]

The experiments on the action of light on iron pentacarbonyl under varied conditions have resulted in new and interesting observations, and approximate measurements of the velocity of the reaction induced by light have been made and compared with that of other reactions induced by light.

The action of heat on solid iron carbonyl, which we described in our former communication as producing an intense green colour, which colour Dr. Mond stated that he had observed casually, has been further examined, and the experiments now described have led to the discovery of a new compound of iron and carbon monoxide, iron tetracarbonyl, which forms dark green crystals of remarkable stability, exhibiting some very striking properties.

Action of Light on Iron Pentacarbonyl.

It was shown in the former communication that the action of light on iron pentacarbonyl alone or in solution in solvents, with the exception of nickel carbonyl, is represented by the equation

$$2Fe(CO)_5 = Fe_2(CO)_9 + CO.$$

Carbon monoxide is evolved and diferro-nonacarbonyl, an orange red crystalline compound, is produced and separates out. When pyridine was.

* 'Roy. Soc. Proc.,' A, 1905, vol 76, p. 558.

used as solvent, the diferro-nonacarbonyl remained in the deep red solution unless very much iron pentacarbonyl had been used, when some crystals were deposited.

The fact that solid is not deposited from a pyridine solution of iron pentacarbonyl under the action of light is attributed* to the solubility of the diferro-nonacarbonyl in pyridine, since it was shown that solid was deposited when the solution contained more than 50 per cent. of the pentacarbonyl. This has been confirmed by using a saturated solution of the diferro-nonacarbonyl in pyridine as solvent for the pentacarbonyl. A 20-per-cent. solution of iron pentacarbonyl in this mixture, on exposure to light for a long time, deposited crystals. Owing to the deep colour of the solution, the action is naturally a very slow one. A 20-per-cent. solution of iron pentacarbonyl in pyridine alone would not have deposited any of the solid.

When nickel carbonyl was used as solvent, no change occurred; the solutions were of a much paler colour than solutions of the same concentration in other solvents, and it was suggested that the two carbonyls united to form an unstable compound {$Fe(CO)_5Ni(CO)_4$} which was analogous to $Fe_2(CO)_9$ and was unaffected by light.

Also it was shown that above 60° C. light had no apparent action on solutions of iron pentacarbonyl, and that the reaction induced by light was reversed in the dark.

The later experiments were directed towards confirming and extending the above observations.

Action of Light on Iron Pentacarbonyl at Higher Temperatures.

In the former communication (p. 574) it was stated that if iron pentacarbonyl or its solutions in ether or petroleum ether were heated to any temperature between 60° and 100° C. while exposed to light, then no separation of solid occurred, even after long exposure and subsequent cooling in the dark.

This remarkable behaviour has been further confirmed by exposing tubes to light while immersed in the vapours of various liquids and observing whether solid was deposited or not, while hot or after cooling in the dark, and also by using tubes provided with a manometer of the type used for the velocity measurements described below. Usually, petroleum ether solutions, containing about 10 per cent. by volume of iron pentacarbonyl, were used; ether solutions were also used.

In ether vapour, 30° to 35° C., solid is slowly deposited, and the manometer shows an increase of pressure. On bright days, an appreciable amount of solid had formed after five minutes.

* *Loc. cit.*, p. 575.

In the vapour of petroleum ether, 45° to 50° C., the solid was more slowly formed, but in half an hour on the same day a distinct amount of crystalline deposit had formed, and the manometer again indicated an increase of pressure.

In acetone vapour, 56° C., no solid was deposited after exposure for five hours to bright sunlight, no increase of pressure was noticed, and no solid was deposited when the tube was allowed to cool in the dark.

In chloroform vapour, 61° C., no change was observed after six hours' exposure to bright sunlight, no solid separated when the tube was cooled in the dark, and the manometer showed that no increase of pressure had occurred.

That the deposition of solid is a delicate and trustworthy indication of any change is proved by the fact that whenever any solid could be observed the manometer indicated an increase of pressure. The solid is extremely sparingly soluble in the two solvents, petroleum ether and ether, and so is deposited as soon as formed. Further, above 46° C., the solid is gradually decomposed, as will be described later, producing a green solution; no trace of this colour was ever observed in the tubes exposed to light at any temperature between 50° and 100° C., provided they contained no solid before they were heated. An experiment was made in which a solution of iron pentacarbonyl containing a little of the solid diferro-nonacarbonyl was heated to 56° C. and then exposed to light. A green colour was produced, but no solid was deposited after several hours.

It is noteworthy that neither on bright days in December nor in July could we observe any decomposition at temperatures above 56° C.; that is, no definite shifting of the transition temperature due to the difference in the intensity of the light could be observed.

These experiments will be discussed later, when the experiments on the reverse reaction have been described.

Approximate measurements of the velocity of the reaction were made in solutions in petroleum ether and in pyridine at two concentrations, and the rate in the two solvents compared. Since no artificial light had been found to effect the change at all rapidly, it was necessary to depend on sunlight, the intensity of which naturally varied considerably. Tubes of the same size were made to hold the solutions, and these were filled with solutions of arbitrary concentrations which were in the ratio of 2 : 1, so that information as to the "order" of the reaction might be obtained. These tubes were sealed on to a capillary tube, closed at the other end and containing a small pellet of mercury; measurements of the movement of this mercury index enabled us to determine the pressure inside the tubes. The tubes were set

side by side in a glass tank of water and exposed to direct sunlight and examined at intervals until no further change took place. Calculation of the fraction of the whole decomposed x/a, where a represents the final increase of pressure and is a measure of the initial concentration of the iron carbonyl, and x is the increase of pressure at any time and is a measure of the amount of decomposition that has taken place, shows clearly that the reaction proceeds as one of the " first order," since it will be seen that the fraction for each concentration is the same within as narrow limits as could be expected in the circumstances. The agreement is naturally not good at the beginning, since the solution must become saturated with the gas. It is probable that great supersaturation is prevented in the case of petroleum ether by the separation of solid; but in the case of pyridine, where no solid separates, this disturbing effect, which tends to make x/a too small at the beginning, is much greater, and good agreement is only obtained near the end of the reaction.

Another fact must also be taken into consideration as affecting the result: in the case of petroleum ether more solid separates from the more concentrated solution than from the other; in the case of pyridine it acquires a deeper colour, so that in both cases less light penetrates the more concentrated solution; in both cases, therefore, the amount of change is relatively less in the more concentrated solution towards the end. This is shown by the greater values of x/a for the dilute solution near the end.

The following two sets of experiments are sufficient to indicate the kind of result obtained:—

I.

Solvent—Petroleum Ether.

Time.	A. Concentration 2.		B. Concentration 1.	
	Pressure.	x/a.	Pressure.	x/a.
	atmos.		atmos.	
2 mins.	1·01	0·001	1·02	0·004
12 ,,	1·30	0·033	1·07	0·014
22 ,,	1·72	0·079	1·30	0·060
32 ,,	2·25	0·147	1·47	0·094
42 ,,	2·46	0·16	1·81	0·16
55 ,,	2·70	0·19	2·05	0·21
112 ,,	3·86	0·32	2·69	0·34
142 ,,	4·26	0·36	2·80	0·36
182 ,,	4·76	0·41	3·25	0·45
247 ,,	5·40	0·47	3·55	0·51
28 hours	7·36	0·70	4·33	0·67
2 days	8·1	0·78	5·2	0·84
∞	10·1	1·0	6·0	1·0

II.

	Solvent—Pyridine.				Solvent— Petroleum Ether.	
Time.	**C. Concentration 2.**		**D. Concentration 1.**		**E. Concentration 2.**	
	Pressure.	x/a.	Pressure.	x/a.	Pressure.	x/a.
	atmos.		atmos.		atmos.	
5 mins.	1·00	—	1·00	—	1·03	0·014
7 ,,	1·00	—	1·00	—	1·10	0·014
10 ,,	1·03	—	1·01	—	1·17	0·023
20 ,,	1·13	—	1·02	—	1·25	0·034
30 ,,	1·16	—	1·03	—	1·47	0·064
50 ,,	1·31	—	1·06	—	1·92	0·126
70 ,,	1·49	—	1·12	—	2·80	0·24
85 ,,	1·60	—	1·24	—	3·02	0·27
105 ,,	1·67	0·13	1·33	0·093	3·13	0·28
135 ,,	1·81	0·15	1·46	0·13	3·57	0·35
175 ,,	2·47	0·28	2·21	0·34	4·41	0·47
255 ,,	3·18	0·43	2·43	0·40	5·00	0·55
325 ,,	3·35	0·46	2·70	0·48	5·30	0·58
26 hours	4·78	0·76	3·47	0·70	5·78	0·65
52 ,,	5·12	0·81	4·07	0·86	6·83	0·80
∞	6·09	1·00	4·56	1·00	8·35	1·00

A tube set up in precisely the same way with nickel carbonyl as solvent showed during several months' exposure only very slight changes of pressure, which were due to temperature changes.

In order to compare the decomposition of iron carbonyl with other reactions induced by light, we compared the rate of evolution of gas from a solution of iron pentacarbonyl in petroleum ether with that from a solution of ferric chloride and oxalic acid. The latter action, which has been examined by Lemoine,* proceeds according to the equation $2FeCl_3 + H_2C_2O_4 = 2FeCl_2 + 2HCl + 2CO_2$, is exothermic, and at the ordinary temperature only takes place under the influence of light.

For the purpose of the approximate comparison, equimolecular solutions of iron pentacarbonyl in petroleum ether and of ferric chloride were used. In order to make the latter reaction approximate more nearly to a reaction of the " first order," two molecular proportions of oxalic acid were used (more cannot be added, since the solution then changes its colour and ferrous oxalate is deposited during the later stages).

Both solutions are yellow, but the colour of ferric salt solution is much deeper than that of the iron carbonyl at the same molecular concentration, hence the comparison is not quite fair, since the amount of change is proportional to the light absorbed, and the latter solution absorbs more light.

* 'Ann. de Chimie et de Phys.,' 1895, [7], vol. 6, p. 433.

Two solutions were used, containing respectively 4 per cent. and 10 per cent. of iron carbonyl, and the rate of change compared with two ferric chloride and oxalic acid solutions of corresponding equimolecular concentrations.

The solutions were placed in tubes of the same size, which were placed side by side in a tank of water, and the gases evolved were collected over glycerine.

The volume of gas evolved from the ferric salt solutions is twice that evolved from the corresponding iron carbonyl solutions.

The ferric salt solutions were saturated with carbon dioxide before being introduced into the tubes, yet it is probable that the supersaturation of the solution which is set up causes a lag in the evolution of gas at the beginning. Later, the deposition of solid from the iron carbonyl solutions cuts off some of the light and further diminishes the rate of this action as compared with the other.

The results of six sets of experiments show that there is no very pronounced difference in the sensibility to light of the two reactions in the more concentrated solutions, but that in the more dilute solutions the ferric chloride and oxalic acid mixture is the more sensitive.

The following table gives the fractions of the total amount of gas evolved from the solutions during the same time :—

Fe(CO)$_5$, 10 per cent.	Fe, 2·86 per cent. H$_2$C$_2$O$_4$, 4·6 per cent.	Fe(CO)$_5$, 4 per cent.	Fe, 1·12 per cent. H$_2$C$_2$O$_4$, 2·86 per cent.
0·24	0·19	0·12	0·28
0·28	0·25	0·26	0·40
0·31	0·37	0·40	0·67
0·40	0·55	0·65	0·85
0·66	0·75	0·75	0·95
0·71	0·79		
0·82	0·94		

The figures for the dilute solutions do not represent readings taken at the same time as those for the more concentrated solutions.

From the above numbers no very definite conclusion can be drawn, but it is probable that iron carbonyl is more sensitive to light than the ferric chloride oxalic mixture, seeing that the decomposition is nearly as rapid in the former case as in the latter, and the amount of light absorbed by the ferric chloride and oxalic acid mixture is greater than that absorbed by the iron carbonyl solutions.

A rough comparison of the velocity of the decomposition of iron carbonyl with that of the reaction between mercuric chloride and oxalic acid, which was measured by the development of pressure due to the carbon dioxide

showed that the former reaction proceeded very much more rapidly than the latter under the same conditions.

Reversal of the Reaction.

The velocity of the reverse reaction, $Fe_2(CO)_9 + CO = 2Fe(CO)_5$, which proceeds in the dark, was studied by using the same tubes that were used for the examination of the direct action (p. 68). The results show that this is an extremely slow reaction at the ordinary temperature. Tube E, above, containing petroleum ether, had a pressure of 3 atmospheres after three months, so that only 73 per cent. of the gas had been reabsorbed by the solid; after 11 months the pressure was still 1·68 atmospheres, so that 92 per cent. of the products had recombined.

With pyridine as solvent, the reverse action was more rapid at the beginning, but did not proceed so far. Thus, after 15 days in the dark, tube D, containing pyridine, had a pressure of 1·8 atmospheres, representing 51 per cent. recombination, while in the petroleum ether tube E only 28 per cent. recombination had occurred in the same time.

The two tubes, A and B, containing petroleum ether, were used for studying the rate of the reverse reaction at higher temperatures. B was heated in ether vapour. In two days the pressure fell from 6 to 4·1 atmospheres, in five days to 2·8 atmospheres, in 10 days to 1·6 atmospheres, and after 16 days the reversal was complete, the solid had disappeared and the pressure had fallen to 1 atmosphere. Similar results were obtained with other tubes. Attempts were made to study the reverse reaction at higher temperatures; in carbon disulphide vapour (46° C.) the reaction appeared to proceed more rapidly, but development of a green colour showed that already the decomposition of the diferro-nonacarbonyl by heat was beginning, and this naturally vitiated the results.

Results of precisely the same kind were obtained with methylal as solvent. The solid diferro-nonacarbonyl is slightly soluble in the solvent, and on heating gives a red solution—it is therefore intermediate in its behaviour between petroleum ether and pyridine; as in the case of pyridine, the reverse action is also more rapid in the early stages than it is in ether or petroleum ether.

These observations on the greatly increased velocity of the reaction between diferro-nonacarbonyl and carbon monoxide at temperatures little above the ordinary temperature are of great importance in their bearing on the absence of any action of light on iron pentacarbonyl above 56° C.

Iron carbonyl shows no selective absorption, but completely absorbs the more refrangible rays.

It was found by spectroscopic examination of iron carbonyl and its solutions that there was no observable difference in the amount of light absorbed at 15° C., and at 60° or 100° C.

The absence of action of light above 56° C. must be due, therefore, either to a greater stability of the iron pentacarbonyl molecule at higher temperatures or to the displacement of an equilibrium represented by the equation

$$2Fe(CO)_5 \rightleftharpoons Fe_2(CO)_9 + CO,$$
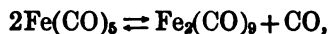
in the direction of the liquid carbonyl at the higher temperatures. The fact that the action of carbon monoxide on the diferro-nonacarbonyl is so much accelerated by an increase of temperature makes it probable that this is the true explanation. Lemoine* has shown that the reaction between ferric chloride and oxalic acid exhibits no appreciable acceleration due to increase of temperature ; the action of light on the silver halides is also little affected by temperature. If the decomposition of iron pentacarbonyl also has no temperature coefficient, which is not improbable, since we were able to observe the action at −180° C., and the reverse action has the normal temperature coefficient of chemical reactions, then the absence of any change at temperatures above 56° C. is easily explained.

This explanation is compatible with the assumption that the decomposition of the pentacarbonyl by light is an exothermic change, so that the reverse reaction must take place with absorption of heat, and an increase of temperature would favour the progress of the endothermic change, *i.e.*, the recombination of carbon monoxide and the diferro-nonacarbonyl.

We are continuing the experiments on these and other chemical reactions induced by light and applying other methods in studying them, the results of which we hope to describe later.

Decomposition of Iron Pentacarbonyl Absorbed in Alumina.

During the course of some experiments on the absorbing power of various substances for gases and vapours, it was found that alumina absorbed 2·5 per cent. of its weight of iron pentacarbonyl from gases saturated with the vapour at the ordinary temperature. On exposing this alumina to light (out of contact with air) it became coloured, first pink, then red, reddish purple, and finally, a dark reddish purple. Experiments showed that during this action carbon monoxide was evolved in approximately the theoretical quantity, if care were taken to shake the alumina frequently so as to expose it all to light.

* *Loc. cit.*

Th solid diferro-nonacarbonyl formed in the alumina possibly forms a kind of "lake" with the alumina. The coloured alumina retains its colour when boiled with pyridine, although alumina will not remove the colour from the red pyridine solutions of diferro-nonacarbonyl. Warm concentrated hydrochloric acid removes the colour, gas is evolved, and ferrous chloride is formed; nitric acid reacts with the coloured alumina in the cold, but sulphuric acid has very little action on it.

Action of Heat on Diferro-Nonacarbonyl.

As stated by Mond and Langer, and confirmed in our previous communication, the solid, when heated alone, breaks up into iron pentacarbonyl, iron, and carbon monoxide. It was observed that the iron pentacarbonyl so produced was coloured green, but that when distilled the green colour was removed from it. This decomposition occurs at about 95° C.

Quantitative experiments were made in which a weighed quantity of the solid was placed in a porcelain boat and heated in a stream of hydrogen to a temperature of about 100° to 120° C. by means of a toluene or an air bath; the volatile iron pentacarbonyl was thus carried off as vapour and passed through a glass tube, bent twice on itself and heated in an air bath to a temperature of about 200° C. The boat and the coiled tube were weighed after the experiment, and so the amount of left iron and the amount of iron deposited from the volatile carbonyl were determined. The boat was then heated in a current of oxygen until there was no further change of weight and so a second determination of the iron made as ferric oxide.

The following are typical experiments performed in this way :—

gramme.		gramme.		gramme.	
0·2981 Fe$_3$(CO)$_9$	gave	0·0754 Fe	in tube and	0·0223 Fe	in boat
0·4505	„	0·1211	„	0·0378	„
0·6555	„	0·1215	„	0·0725	„

It is evident that this method does not give consistent results, and even if it did it would probably give values for the iron deposited in the bent tube from the iron pentacarbonyl that were too high, since it has been shown that the iron so deposited always contained carbon.

Other experiments were then made in which the iron pentacarbonyl was collected and weighed.

A weighed quantity of diferro-nonacarbonyl was placed in one limb of a U-shaped tube, which was then exhausted and sealed. This limb of the tube was heated and the iron pentacarbonyl which was formed was condensed in the other limb by cooling this in liquid air. The iron pentacarbonyl and the

residue left in the other limb of the tube were weighed. The residue was found to be iron in such a finely divided state that it was pyrophoric.

The following experiments are typical. In the first experiment the solid was heated to 100° C. and in the second to 110° to 115° C.

<div align="center">

gramme.   gramme.   gramme.

0·685 $Fe_2(CO)_9$ gave 0·567 $Fe(CO)_5$ and 0·055 Fe

0·587   „   0·453   „   0·039 „

</div>

In the former communication it was stated that the decomposition might be represented by the equation

$$2Fe_2(CO)_9 = 3Fe(CO)_5 + Fe + 3CO.$$

The above results confirm this, since the amounts of $Fe(CO)_5$ formed on this view would be 0·583 and 0·503 gramme respectively, and the amounts of iron would be 0·053 and 0·045 gramme respectively.

Since it is shown later that, by the action of heat on diferro-nonacarbonyl in presence of solvents below 100° C., a compound, $Fe(CO)_4$, is produced, it is quite possible that the decomposition was produced in two stages, represented by the equations

$$2Fe_2(CO)_9 = 2Fe(CO)_5 + 2Fe(CO)_4$$

and

$$2Fe(CO)_4 = Fe(CO)_5 + Fe + 3CO.$$
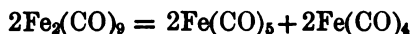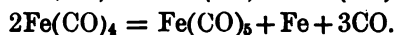
This view is supported by the fact that when diferro-nonacarbonyl is heated to 100° C. in a tube filled with carbon dioxide and fitted with a small mercury index manometer, at first the solid is decomposed with formation of a green liquid without any appreciable development of pressure, but as the heating is continued, pressure is gradually developed, iron is formed, and the green colour disappears.

When heated to 100° C. with carbon monoxide under a pressure of 75 atmospheres, the solid is at once converted into liquid iron pentacarbonyl and no green colour is produced. This shows that the recombination of carbon monoxide with the diferro-nonacarbonyl is favoured by pressure and the formation of the green compound usually produced is prevented in this way.

These facts are here restated and supported by further evidence in order that they may be compared with the results of experiments on the action of heat on diferro-nonacarbonyl in the presence of solvents.

When the cystals of diferro-nonacarbonyl are heated with a solvent such as ether or toluene, change begins at a much lower temperature, below 60° C., and the liquid acquires a dark green colour (as stated above, the green colour is developed slowly, even at 46° C.). When enough of the solvent is present

the whole of the solid dissolves and no iron or other solid substance is produced; the solution has such an intense colour that it is opaque, except in very thin layers.

It is clear, therefore, that we have here a different reaction to deal with.

The green solutions on exposure to light lose their colour and deposit the orange crystals of diferro-nonacarbonyl and a small quantity of a black solid.

By carrying out experiments in a closed tube filled with inert gas and fitted with a mercury manometer, it was shown that no change of pressure was caused by the action of heat or diferro-nonacarbonyl; hence no gas can have been evolved. Long continued heating, however, causes a disappearance of the green colour, and slight pressure is developed.

Similar results were obtained when benzene, petroleum ether, brombenzene or iron pentacarbonyl was used as solvent.

When pyridine, alcohol, acetone or acetonitrile was used as solvent, the solution obtained was not green, but some shade of red or brownish red, but again no gas was evolved.

When nickel carbonyl was used as solvent, the solution obtained was yellow, with only the faintest trace of green colour, a black solid was left, probably iron, and gas was evolved.

With chloroform, ferrous chloride was produced, so that the solvent had entered into the reaction; solid products were also produced when nitrobenzene was used as solvent, and with ethyl acetate or methyl aniline a greenish brown solution and a solid were produced.

The green solutions in toluene, ether or petroleum ether were found in some cases to deposit beautiful green crystals, which, when separated, were found to contain iron and carbon monoxide and to redissolve in the solvent to give a green solution.

After numerous trials, the best conditions for the separation of the maximum amount of these crystals were found, and the following summarises the process used for their preparation.

The solid diferro-nonacarbonyl was sealed up in a tube, the air from which had been displaced by carbon dioxide, with toluene in the proportion of 1 gramme of the carbonyl to 20 c.c. of toluene. The tube was then heated gradually, with occasional shaking, to about 95° C. and kept at that temperature until all the reddish yellow solid had disappeared, the tube being meanwhile shaken from time to time. If shaking is omitted or if the tube be heated to too high a temperature or for too long a time, a quantity of dark coloured powder is formed, but with care this may be almost entirely avoided.

The tube is then allowed to cool slowly, when fairly large crystals of the

green compound separate from the solution and, after washing with the solvent and drying in a desiccator, were used for analysis.

The yield of the green crystals obtainable is only about 20 per cent. by weight of the diferro-nonacarbonyl used.

The carbon monoxide was determined by combustion, care being taken to heat the boat long enough to oxidise any carbon that may have been retained in the iron. In this case the iron almost entirely remains in the boat and, in some cases when there was no observable loss, good determinations of the percentage of iron·were obtained by weighing the ferric oxide; in other cases there was obviously a loss, indicated by deposition of iron on the combustion tube near the boat, and the percentage of iron was low. Independent determinations of the iron were made by decomposing a weighed quantity of the crystals with nitric acid and igniting.

The following results were obtained by these methods :—

(1) 0·1078 gramme gave 0·1118 gramme CO_2 and 0·0513 gramme Fe_2O_3.

(2) 0·1214   „   0·1258   „   „   0·0442   „

(3) 0·1744   „   0·0845   „ Fe_2O_3.

(4) 0·1828   „   0·0868   „   „

	Found.	
	CO.	Fe.
(1)	66·1	33·3
(2)	65·9	—
(3)	—	33·9
(4)	—	33·2
$Fe(CO)_4$ requires...	66·66	33·33

The compound is, therefore, *iron tetracarbonyl* or some polymer of this.

The decomposition of diferro-nonacarbonyl in presence of solvents such as toluene and ether is probably to be represented by the equation

$$Fe_2(CO)_9 = Fe(CO)_5 + Fe(CO)_4.$$
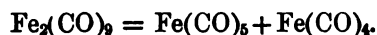
Further evidence in support of this was obtained by carrying out the decomposition in tubes filled with carbon dioxide and fitted with a mercury manometer. No change of pressure was produced by the decomposition. On exposing the tubes, after heating and now containing a green solution, to light, the orange crystals of diferro-nonacarbonyl were deposited and pressure was produced, showing that during the action of heat iron pentacarbonyl had been produced.

Iron tetracarbonyl crystallises in short, dark green, lustrous prisms, the density of which was determined by the flotation method in a mixture of ethylene dibromide and alcohol, in both of which the compound is almost

insoluble and was found to be 1·996 at 18° C.; the molecular volume is therefore 84. If we suppose that a molecule of $Fe_3(CO)_9$ (molecule volume 174) decomposes into a molecule of solid iron pentacarbonyl (molecule volume 128) and a molecule of the new iron tetracarbonyl, 174 volumes become 212 and there is consequently an expansion of 38 volumes, or about 22 per cent.

Iron tetracarbonyl is a substance of remarkable stability. On heating to about 140° to 150° C. it decomposes into carbon monoxide and iron. When heated under a pressure of 150 atmospheres of carbon monoxide it underwent no visible change until a temperature of 129° C. was reached, and then only turned slightly brown; it was not found possible to reconvert it into iron pentacarbonyl.

Reactions of Iron Tetracarbonyl.

The compound is not attacked by a concentrated solution of hydrochloric acid even on boiling; it is attacked by cold concentrated nitric acid, but only by concentrated sulphuric acid when heated. In the last case carbon monoxide and *ferrous* sulphate are produced. Aqueous solution of alkalies, whether hot or cold, had only a very slight action on the compound.

Molecular Weight.

Iron tetracarbonyl is soluble in many organic solvents, to which it imparts an intense colour; as it appeared to be decidedly soluble in benzene, it was thought that a molecular weight determination might be made by the cryoscopic method.

On examining the solubility, however, it was found to be small, only about 4 per cent. in benzene and much less in acetic acid and alcohol.

Attempts were, however, made to determine the molecular weight, and proved definitely that the molecular weight must be very high.

For instance, a solution of 0·031 gramme of the compound in 12·88 grammes of benzene had a freezing point only 0·003° C. below that of the solvent.

Now if the molecule were $Fe(CO)_4$(168) the depression of freezing point should be 0·076° C., so that the molecule would appear to be of the order of $\{Fe(CO)_4\}_{20}$, or, at any rate, the compound is a polymer consisting of many $Fe(CO)_4$ units.

Behaviour of Iron Tetracarbonyl towards Solvents.

Iron tetracarbonyl dissolves in benzene, toluene, petroleum ether, ether, acetonitrile, ethyl acetate, methyl and ethyl aniline, acetone, nickel carbonyl, and iron pentacarbonyl to give solutions of a dark green colour.

It is much less soluble in ethyl acetate and ether than in the hydrocarbons and carbonyls.

The solutions in the above solvents are all stable to heat at 100° C. for short periods, but the colour gradually disappears and iron is deposited if the heating be long continued. This decomposition is quickly completed at 140° C.

The iron tetracarbonyl can be recrystallised easily from toluene, petroleum ether or nickel carbonyl, when due care is taken to prevent oxidation, to which the solutions are very sensitive.

Pyridine, on the other hand, dissolves iron tetracarbonyl quickly and gives a green solution, which on standing for a few minutes turns red, which change of colour is brought about rapidly by warming.

Alcohol behaves similarly; only a faint green colour is obtained, as the substance is very sparingly soluble in alcohol; this solution becomes red on boiling. Solutions of the iron tetracarbonyl in the solvents, in which it forms green solutions when mixed with pyridine in sufficient quantity, turn red on standing.

It is probable, therefore, that the iron tetracarbonyl when dissolved in pyridine exists in a different molecular state from that in which it exists in the green solutions, that is, it is dissociated into simpler molecules or is combined with the solvent. The same is true of solutions in alcohol. Now it was found that acetonitrile and acetone also gave red solutions instead of green when heated with the diferro-nonacarbonyl. Presumably the iron tetracarbonyl is present in these solutions in the same molecular state as in the pyridine solutions, but the effect of these solvents is only strong enough to bring about the conversion of iron tetracarbonyl into this state at the moment of its formation and not at a later stage.

It is noteworthy that iron tetracarbonyl dissolved in either nickel carbonyl or iron pentacarbonyl gives a green solution; hence, it follows that this solid iron tetracarbonyl is different from the hypothetical $Fe(CO)_4$, which it was suggested in our former communication[*] was the first product of the action of light on iron pentacarbonyl, and which then combined with this to form $\{Fe(CO)_5Fe(CO)_4\}$ or diferro-nonacarbonyl.

The green solutions of iron tetracarbonyl exhibit a characteristic absorption band in the yellow, while the red solutions show no selective absorption.

Action of Light on Iron Tetracarbonyl.

The green solutions gradually lose their colour on exposure to light, and a metallic looking solid, probably iron, is deposited. The change is very

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[*] *Loc. cit.*, p. 576.

slow and the solutions were too dilute to allow of the detection of evolved gas with certainty: a small amount of a reddish solid, probably ferric oxide, was frequently observed, which was due to oxidation by traces of dissolved oxygen.

The red solution in pyridine appears to be quite stable to light; no change can be observed after long exposure.

Experiments on the Length of the Cathode Dark Space with Varying Current Densities and Pressures in Different Gases.

By Francis William Aston, A.I.C., Research Scholar at the University of Birmingham.

During some experiments with various types of vacuum tubes the author was led by the behaviour of one in particular to believe that conditions were possible under which the length of the cathode dark space might be an accurately measurable quantity.

This tube is shown in fig. 1. The aluminium disc cathode K is movable and exactly fits the tube containing the anode A. If it is placed to the right in the bulb and a current from a coil passed, the dark space assumes a highly indefinite and irregular form, such as is indicated. If,
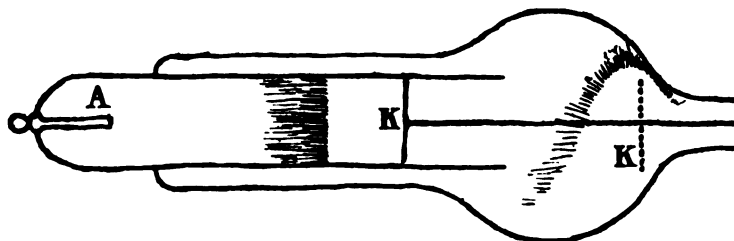
Fig. 1.

however, K is slid to the left, right into the tube containing A, the boundary of the negative glow becomes a very definite plane parallel to the cathode, its distance from the cathode being the same for all positions of the latter so long as it is inside the tube and the current from the coil kept constant.

These conditions, viz.: that the cathode is a flat plate and fills the cylinder of the discharge tube—have a great advantage over those under which the previous measurements were made by Ebert,[*] as the edge of the negative glow is a plane and can be seen without looking *through* the negative glow.

The first series of measurements were made with a tube of this type shown in fig. 2, the cathode being an iron plate 4 cm. diameter. The tube

Fig. 2.

was connected to a special form of Töpler pump of small capacity and to a Rayleigh manometer[†] reading to 0·001 mm. A very large coil working at a low amperage was used in order to keep the current as constant as possible. The length D of the dark space was measured by means of a telescope cathetometer, and its relation to the pressure was plotted for hydrogen, nitrogen, air, and oxygen. In all these gases for values of D between 0·2 and 2 cm. the appended curves (Table A) show the relation to be approximately linear,

Table A.

y = Dark space in M.M.
x = Reciprocal of Pressure.
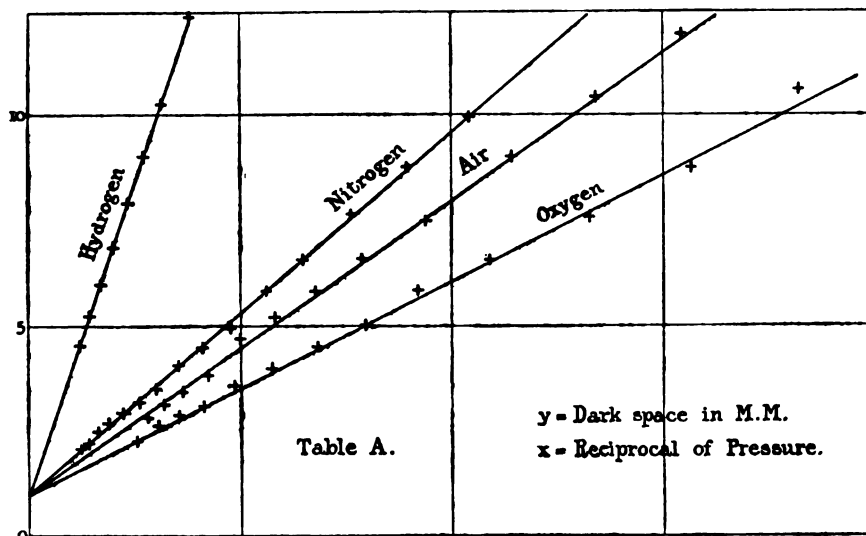
satisfying the equation D = A + B/P, where A = about 1 mm. for all the gases, B being a constant for any particular gas and proportional not to its " mean free path," but roughly to the velocities of its ions found by Zeleny[‡]

* Ebert, ' Wied. Ann.,' vol. 69, pp. 200, 372, 1899.
† Rayleigh, ' Phil. Trans.,' A, vol. 196, p. 205, 1901.
‡ Zeleny, ' Phil. Trans.,' A, vol. 195, p. 193, 1900.

and the coefficient of diffusion of its ions by Townsend.* This very interesting result led to the fitting up of apparatus by which experiments on D could be made with the current under control, and it is with this apparatus, the results obtained, and their possible bearing on the nature of the dark space, that this paper deals.

The four variables to be measured were current (c) flowing through the tube, potential difference between electrodes (V), pressure of the gas (P), and length of dark space (D).

Current.—The coil was replaced by a battery of 480 accumulators applied direct to the tube which, when in series with the city mains, commanded a potential of over 1000 volts. The current was controlled by a very large variable liquid resistance, consisting of tubes containing water or a solution of copper sulphate with movable electrodes of platinum or copper respectively.

It was measured by shunting it through a standard resistance connected with a sensitive D'Arsonval galvanometer, which was carefully calibrated by known currents. With 1 ohm in shunt and 1 milliampere passing through main circuit, the galvanometer gave a deflection of 25 divisions, so that each division = 120,000 electrostatic units.

Potential.—Two Kelvin electrostatic voltmeters were employed, having a total range of 200 to 950 volts.
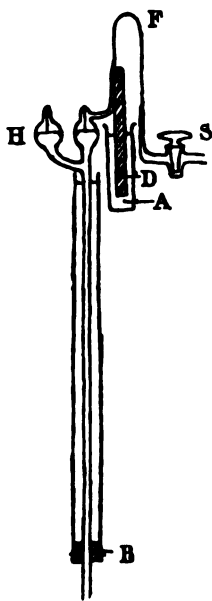
FIG. 3.

Pressure.—In order to obtain the low pressures, a special form of Töpler pump was used at first, but subsequently replaced by a cocoanut charcoal absorption tube cooled in liquid air, by which means mercury vapour was eliminated from the gas under consideration. This method of obtaining vacua was found' extremely convenient and rapid, it being possible by its aid to reduce the pressure in the large and complicated apparatus of volume considerably over 1 litre from several millimetres to 0·01 mm. *in a few minutes.*

Measurement of the pressure was made by means of a Rayleigh manometer.† In order to eliminate the vibration of the building, which during working hours quite masked the sensitivity of the instrument, after many trials the suspension shown in fig. 3 was adopted. The long stalk of the manometer was passed through a rubber bung B which closed the lower end of a wide glass tube fixed to the tilting table and filled

* Townsend, ' Phil. Trans.,' A, vol. 193, p. 129, 1900.
† *Loc. cit.*

with engine oil, forming a jacket which effectually damped all horizontal vibrations transmitted to the head of the manometer H through the stalk. One member of the head was connected to the stop-cock S by means of a thin drawn out glass tube F, the thicker part of which, near the head, was clamped to a small billet of wood D immersed in an oil bath A, the system forming a dash pot which successfully isolated the head from horizontal vibration derived from stop-cock S which was fixed to the tilting table and connected by a flexible glass tube to the apparatus. The zero of the manometer, *i.e.*, the reading when pressure $= 0$ in the right-hand bulb, was obtained by evacuating the head to the highest degree possible with the Töpler pump while the level of the mercury was below the junction of the bulbs. The mercury was then allowed to rise and the reading taken as zero. A value of the zero could now be obtained when required without the necessity of lowering the mercury below the junction, simply by pumping until the instrument showed no further alteration, for, since the pressure in the left-hand bulb is exceedingly small, and its volume from the construction of the apparatus practically constant, its variation during any set of readings must be entirely negligible.

The actual adjustment of the points was performed with the help of a microscope and mirror arranged as indicated in fig. 4, by means of which both points and both reflections could be seen in the field at once, a very great advantage in making the close comparison between them. The scale of the manometer was so arranged that each division $= 0.005$ mm.
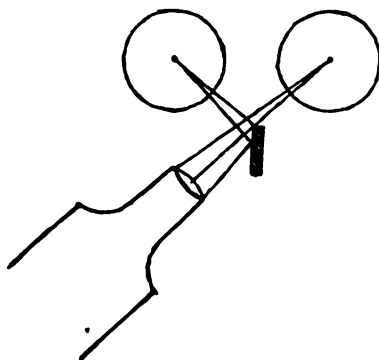
Fig. 5.

Fig. 4.

pressure, or 6.671 dynes per square centimetre. The instrument was read to 0.1 of a division. A zero was frequently taken, as it varied considerably from time to time, owing to the movements of the supports of the manometer and its reading telescope. For all gases, except hydrogen, the zero was precisely the same, whether the exhaustion was performed by

liquid air or the Töpler pump. In the case of hydrogen the absorption at very low pressures by the cooled charcoal was so slow that the manometer had to be connected to the Töpler pump for a reliable zero to be obtained.

Length of Dark Space.—The best way of measuring this quantity was found to be a simple sighting arrangement consisting of a brass tube 35 cm. long by 4 cm. wide, one end of which was closed by a cap drilled centrally with a small eye hole, the other end being fitted with a V-shaped pointer. This tube was mounted on a sliding scale so as to be always exactly parallel to the cathode while moving perpendicular to it. The reading was taken when the point of the sighter exactly coincided with the edge of the dark space, when the appearance through the eye hole was as shown in fig. 5. In hydrogen, nitrogen, and air the pointer was set at the position where the most marked change in appearance took place, this being so definite—under conditions of current density mentioned below—that with a little practice it could be set to about 0·1 mm. In the case of oxygen the sharpness of the edge was simply amazing; in this gas, even with so large a dark space as 3 cm., the sighter could be set as accurately as to the cathode itself, *i.e.*, to about 0·01 mm. Owing, unfortunately, to serious irregularities in the glass walls of the containing cylinder, no such accuracy applies to the actual measurement of D. These results only hold when the current density is so high that no "positive light" was visible on the anode, *i.e.*, very much higher than that required to cover the cathode with glow. Under these conditions it was found by trial with movable electrodes that *their distance apart, so long as it was considerably longer than the dark space itself, had no measurable effect on either dark space, voltage, or current.* If the anode plate is moved slowly towards the cathode, at the instant their distance apart equals the length of the dark space at prevailing conditions, the discharge alters abruptly in character, flickers and ceases, showing that the negative glow is not only an optical effect of, but an essential factor in, the mechanism of conduction, and that the length of the dark space can be measured, if necessary, by purely electrical means.

Discharge Tube.—The first discharge tube was one of 6·5 cm. diameter, the electrodes being flat aluminium plates, just filling it, 12 cm. apart. The dark space was found to *decrease* with *increased* current density, and so long as its length was small, compared to the diameter of the tube, the following two equations were nearly satisfied :—

$$D = \frac{A}{P} + \frac{B}{\sqrt{c}},\qquad\qquad (1)$$

$$V = \frac{F\sqrt{c}}{P} + E.\qquad\qquad (2)$$

A and F were constants roughly proportional to the velocity of the ions of the gas, B and E constants, and B/E roughly constant for different gases.

Theory of the Dark Space.—These two empirical equations, together with the behaviour of the current with movable electrodes, led the author to the conclusion that, at any rate as an approximation, *the dark space may be regarded as a region of positive electrification travelling towards the cathode in which the total positive charge exactly balances the negative charge on the cathode.*

Assume the negative density in the dark space to be negligible. Let ρ = density of positive electricity at a distance x from negative glow, $-\sigma$ = charge per square centimetre on cathode, X = electric force at distance x; then if we take cathode and negative glow as infinite planes a distance D apart—

$$X = 2\pi\sigma + \int_0^x 2\pi\rho\,dx - \int_x^D 2\pi\rho\,dx.$$

By the above hypothesis

$$\int_0^D \rho\,dx = \sigma; \quad \text{thus} \quad X = 4\pi\int_0^x \rho\,dx.$$

Let v = velocity of positive ion ; assume $v = \lambda X$, where λ = velocity in unit field. Also, since at all points c = current density carried by positive ions,

$$\rho v = c, \quad \text{so that} \quad X = c/\lambda\rho ;$$

therefore

$$\frac{c}{\lambda\rho} = 4\pi\int_0^x \rho\,dx.$$

Thus

$$\frac{c}{\lambda\rho^2}\frac{d\rho}{dx} = 4\pi\rho ; \quad \text{hence} \quad \frac{c}{8\pi\lambda\rho^3} = x + \text{const.}$$

As the electric force in the negative glow is negligible, we have finally

$$\rho = \left(\frac{c}{8\pi\lambda x}\right)^{\frac{1}{3}} ; \qquad v = (8\pi\lambda cx)^{\frac{1}{3}} ;$$

$$X = \frac{c}{\lambda\rho} = \left(\frac{8\pi cx}{\lambda}\right)^{\frac{1}{3}} .$$

Let V = fall of potential across dark space, then

$$V = \int_0^D X\,dx = \left(\frac{8\pi c}{\lambda}\right)^{\frac{1}{3}}\tfrac{3}{4} D^{\frac{4}{3}} .$$

If we assume this current carried by the positive ions to be the whole or a constant fraction of the total current passing between the cathode and the negative glow, then—

$$\lambda \propto cD^3 V^{-2}.$$

Townsend* has shown that the coefficients of diffusion of ions are inversely proportional to the pressures. Assuming that this is true for the velocities of positive ions at the range of pressure in these investigations, we should expect from the theory that cD^3PV^{-2} equals an absolute constant for a given gas. It will be seen that if we make c so large that the third terms of the empirical equations (1) and (2) are negligible they satisfy this result.

In the formulation and subsequent testing of the theory above the following phenomenon was of importance. When D was large, the discharge at the cathode had the appearance indicated in fig. 6, there being a ring on the outside of the cathode of thickness varying with D, which did not appear to take part in the discharge at all. The curve of faint glow shown could be easily seen, and a, the distance from the side of the tube to the working part of the cathode, was roughly measured and found to be linear with D, and apparently independent of the nature of the gas. For hydrogen and oxygen $a = 0.35\,D$ for this particular tube. This result appears to be due to the presence of a positive charge on the glass walls in the dark space. Several observations point to the conclusion that only that part of the cathode inside a carries any current, and from this it follows that in order to get a measurement of the true current density in the dark space this edge effect must be eliminated, and, secondly, that if current is carried across the dark space by positive ions, practically all of these must be generated in the negative glow, a result which is corroborated by the behaviour of the tube when the electrodes are moved nearer together.
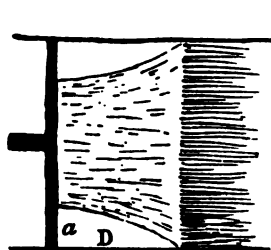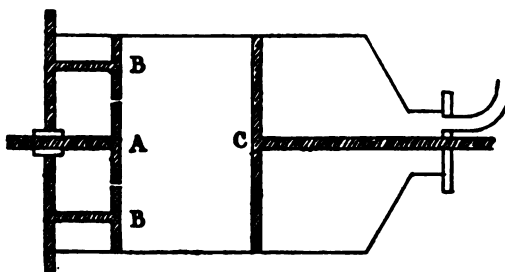
FIG. 6.   FIG. 7.

In order to get rid of this edge effect a large cylindrical bottle (fig. 7) was used, 10·15 cm. in diameter. The cathode was made in two insulated parts, a guard ring BB filling the tube, and a central circular plate A, 4·18 cm. in diameter, both being turned out of the same aluminium plate. The interval between the two was about 0·2 mm., so that when both were

* Townsend, 'Phil. Trans.,' A, vol. 195, p. 259, 1900.

connected to the battery, as shown in fig. 8, the whole behaved exactly as one large plate. That portion of the current passing through A only was sent through the shunt of the galvanometer and read off, and as D was small compared to B this gave a reliable measure of the current density at the middle of the cathode, for so long as the latter is clean and flat there seems no reason to suppose the current density to be other than uniform over the central area remote from the glass walls; in fact, the absolute parallelism of the cathode and negative glow renders such a supposition unlikely.

The area of the working part of the cathode A is 13·73 sq. cm., which gives 8748 electrostatic units of current per square centimetre per division deflection of the galvanometer. As the discharge tube was not perfectly cylindrical, current density above a certain limit—80 divisions for hydrogen, 60 for other gases—could not be employed, as at that point the back of the cathode started discharging through the space between the guard ring and the glass walls. The form of the anode C does not appear to affect the discharge, but for uniformity it was made an aluminium disc filling the tube and parallel to the cathode. The distance between the electrodes in this tube was 17·5 cm.
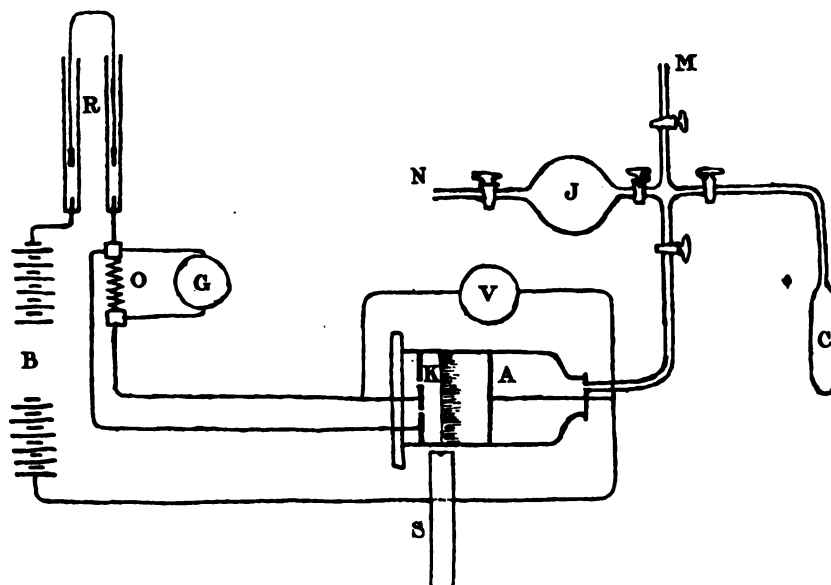
FIG. 8.

Fig. 8 gives a plan of the general arrangement of the apparatus. B, large battery; R, variable liquid resistance ; O, standard shunt; G, D'Arsonval galvanometer; K, "guard ring" cathode; V, static voltmeter; A, anode

S, sighter for measuring dark space; J, bulb containing P_2O_5 and gas in use; C, cocoanut charcoal absorption tube for immersion in liquid air.

The gases, the results of which are given, were: hydrogen from zinc and sulphuric acid; nitrogen from air by absorption by phosphorus; air; and oxygen from a cylinder. They were admitted to the discharge tube perfectly dry and impurities derived from the electrodes, etc., in the tube eliminated as far as possible by heavy discharges and repeated washings with fresh gas. The resistance R was adjusted till the galvanometer indicated the current required, when the dark space and voltage were read off as quickly as possible. The pressure generally varied slightly during a set of readings, sometimes increasing and sometimes decreasing, the number quoted being the mean.

The results are given in Tables I, II, III, IV (pp. 93—95), where it will be seen that cPD^3V^{-2} is roughly constant for each gas. If we assume $\lambda \times$ absolute pressure $= v_0$, the velocity of a positive ion in a field of 1 electrostatic unit per centimetre at a pressure of 1 dyne per square centimetre, then, from theory,

$$v_0 = \frac{8\pi c P}{V^2} \cdot \tfrac{4}{3} D^3,$$

where everything is measured in absolute electrostatic units. Thus v_0 for oxygen is $2 \cdot 29 \times 10^6$. Reducing this value to that for a field of 1 volt per centimetre and a pressure of 1 atmosphere, we can compare the ionic velocities so found with those determined by Zeleny.* They are as follows, in centimetres per second :—

Gas.	Velocity (Zeleny).	Velocity from dark space.
Hydrogen	6·70	7·7
Nitrogen	—	0·79
Air	1·36	0·78
Oxygen	1·36	0·76

These results agree quite as well as could be expected, considering that the gas in these two methods was at pressures of 760 mm. and below 0·5 mm. respectively, and seem to suggest but little alteration in e/m for positive ions over this very large range of pressure. As they are obtained by giving c the value of the whole current density given by the galvanometer reading, they represent maxima.

We have at present no evidence to show the relative percentage of current carried by + and − ions respectively in the dark space; the difference between their mechanical energies can, however, be very prettily shown by

* *Loc. cit.*

the following experiment. A tube was made, in which two similar light mica mills, with vanes *uuu* and *lll*, respectively set at 45° to the cathode, were
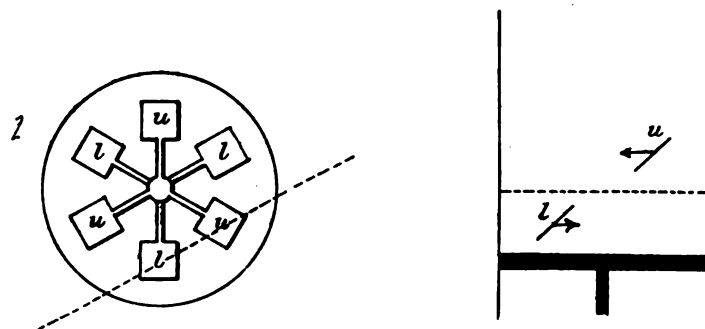
Fig. 9.

mounted one above the other, so that when a moderate current was passed, the lower mill *lll* was wholly inside, the upper *uuu* wholly outside the dark space. Under these conditions the vane *u*, situated in the negative glow, showed a barely perceptible motion to the left, while the one in the dark space rotated violently in the opposite direction. The momentum carried by the current towards the cathode is therefore greatly in excess of that carried away from it.

The phenomenon, described by Wehnelt,[*] of an obstacle in the dark space casting shadows both ways, is very beautifully shown by the lower mill, its moving shadow on the surface of the cathode being very clear, while, if its rotation is not too rapid, very distinct interference with the slow motion of the upper mill can be detected, doubtless due to the intermittent cessation of the corpuscular bombardment, causing the rotation of the latter.

Still assuming, for the sake of simplicity, that all the current is carried by positive ions, we may calculate, by the theory above, the absolute values of v and ρ at any point in the dark space. Thus in hydrogen with a dark space of 1 cm. and a current of 70 divisions deflection (= about 0·2 milli-ampere per square centimetre) at the surface of the cathode,

$$v = 8\cdot5 \times 10^6 \text{ cm./sec.}$$

In oxygen with the same dark space and a current giving 40 divisions deflection, at the surface of the cathode,

$$v = 4\cdot0 \times 10^6 \text{ cm./sec.}$$

These velocities are about 1/10 those measured directly by Wien[†] at a very much lower pressure and higher potential for Canal-Strahlen.

* Wehnelt, 'Wied. Ann.,' vol. 67, p. 421, 1899.
† Wien, 'Wied. Ann.,' vol. 65, p. 440, 1898.

As the velocities quoted above are maxima for the positive ions in the dark space under the conditions mentioned, and about one thousand times less than the smallest velocity measured for cathode rays, the fundamental assumption made in the theory that at any point in the dark space the density of the negative ions is negligible compared with that of the positive ones seems to be upheld by these numbers, as it is also by the results of some determinations of the number of negative ions present at various points along the discharge, made by Professor J. J. Thomson.[*]

In oxygen with D = 1 cm., C = 40 divisions deflection at a point 1 mm. from negative glow, $\rho = 0.3$, or adopting the accepted values of e and N, one + ion to about 500,000 molecules.

The limits of the length of the dark space appear to be purely dependent upon the dimensions of the discharge tube and the pressure of the gas. Thus, in the tube shown in fig. 7, a dark space of the order of 10 cm. could be observed, while in a very small one, in which the cathode was an aluminium plate only 0.5 mm. wide, a dark space was measured of about 0.005 cm. (in air at about 20 mm. pressure); one of similar dimensions could be clearly seen when a current was passed between platinum wires in the flame of a small gas jet.
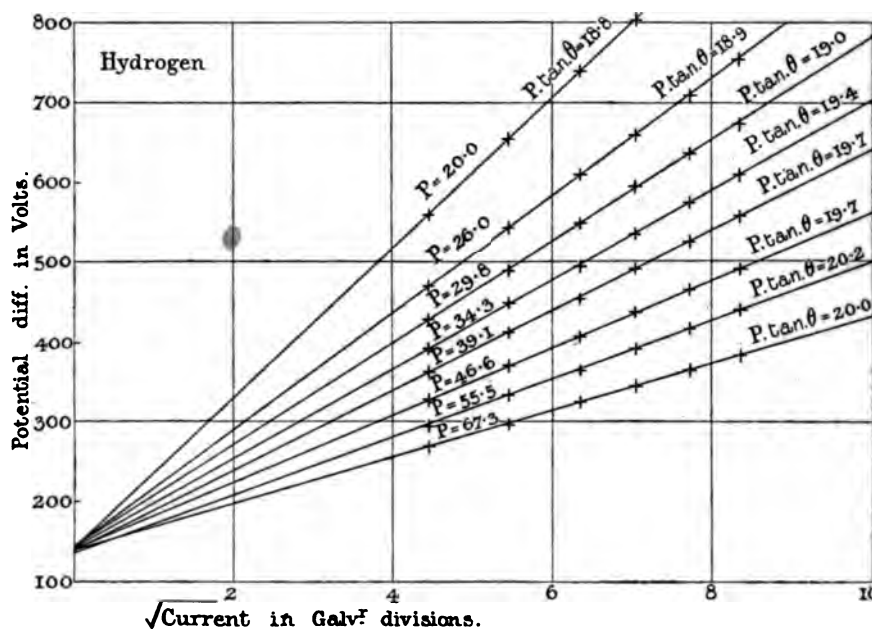
The relations between current and voltage for the discharge from the

* J. J. Thomson, 'Phil. Mag.' Ser. vi, vol. 1, p. 361, 1901.

"guard ring" cathode are shown in the foregoing curves. It will be seen that at low pressures the approximation to the equation

$$V = FP^{-1}\sqrt{c} + E$$

is very close indeed, particularly for hydrogen.

The following are the mean values of F in absolute electrostatic units and of E in volts:—

Gas.	F.	E.
Hydrogen	0·00465	144
Nitrogen	0·00194	230
Air	0·00191	230
Oxygen	0·00143	290

E appears to be nearly the same as the cathode fall for aluminium cathodes in those gases in which it has been determined. Since, by theory, $V \propto vD/\lambda$, assuming $\lambda \propto$ mean free path in the same gas velocity of $+$ ions $\times$ number of collisions of corpuscle in dark space = a constant + a variable, which seems to suggest that the secondary ions formed in the dark space are the ones by which the ionisation in the negative glow is maintained.

The author offers the following suggestions, of a purely speculative nature, to account for the existence of the dark space and its behaviour:—

That, under the impact of positive ions, the aluminium cathode is capable of discharging corpuscles with sufficient velocity to ionise the gas, their numbers and ionising effect at the negative glow being functions of the velocity and mass of the positive ions and the length of the dark space.

That above a certain minimum current density, which has been shown to be a function of the pressure,* the gas, under a corpuscular bombardment of a certain intensity, gets into an unstable state comparable to that of a flame in which the available ions are so numerous that the gas behaves much as a liquid electrolyte, the electric force at any point being very small; this is the negative glow.

It is conceivable that in this flame state the colliding ions of opposite sign do not always recombine instantly and completely to form neutral molecules, but may do so partially, forming kinetic systems requiring but little energy from colliding corpuscles and transfer of charge among themselves to support their active existence. Such systems would probably fly to pieces in a very small electric field, so that the instant one diffuses across the boundary of the negative glow towards the cathode—a region the field of which has already

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* H. A. Wilson, 'Phil. Mag.,' Ser. vi, vol. 4, p. 608, 1902.

been discussed—it is destroyed, the positive member travelling towards the cathode, while the charge of negative electrification left behind is transferred almost instantaneously by a system of exchanges to the anode which we will suppose in the negative glow.

If the breaking strain of these systems is small and definite, the boundary of their existence will be sharply defined, and in oxygen this is the case to a very striking degree ; in fact, it is the *extreme* sharpness of the edge of the negative glow in this gas which seems to necessitate some such explanation as this. Further support is given by the presence of brilliant lines in the spectrum of the negative glow, which disappear almost entirely in that of the dark space.

Leaving out of account the current carried from the cathode by the corpuscles, it is plain that equilibrium will be reached when the number of positive ions diffusing past the boundary of the negative glow is just sufficient to maintain the current passing through the tube. This number must certainly be some function of the density of ionisation maintained in that part of the negative glow which in its turn depends on the available energy of the bombarding corpuscles. This last we have assumed to be dependent upon the velocity and mass of the positive ions and the length of the dark space. Hence, for equilibrium, the length of the dark space must adjust itself so that the conditions of impact of the positive ions will give a stream of corpuscles exactly sufficient to supply the ionising energy required in the negative glow at that particular current. This energy, when once the discharge has started, may very well be small, in which case the number of corpuscles discharged by the cathode may be small compared with the number of positive ions striking it, which appears likely to be the case.

Such a theory as the above explains to some extent the unsatisfactory results obtained in measurement of the dark space by previous investigators, and also the remarkable anomalies of conductivity, etc., found in such tubes as the Crookes V-tube, as the cathode in all these cases was so placed that the area of the negative glow and the distribution of the field between it and the cathode were quantities of unmanageable complication.

In conclusion, I wish to express my indebtedness to Professor J. H. Poynting for the means by which the experiments were carried out and for his kind help and advice at every point in the investigation, the mathematical part in particular.

Table I.—Hydrogen.

c = Current in galvanometer divisions.
D = Length of dark space in centimetres.
V = Difference of potential in volts.
P = Pressure in manometer divisions.

c	D	V	$\frac{cD^3}{V^2} \times 10^4$	D	V	$\frac{cD^3}{V^2} \times 10^4$	D	V	$\frac{cD^3}{V^2} \times 10^4$
40	0·857	271	3·43	1·100	304	5·77	1·478	398	8·15
50	0·822	281	3·50	1·062	322	5·77	1·441	428	8·19
60	0·788	291	3·48	1·030	337	5·77	1·423	453	8·44
70	0·770	300	3·54	1·009	354	5·74	1·386	476	8·20
80	0·736	309	3·35	0·987	367	5·71	1·365	499	8·20

$P = 121{\cdot}4$	$P = 72{\cdot}2$	$P = 49{\cdot}5$
$\frac{cD^3P}{V^2} \times 10^4 = 420$	$\frac{cD^3P}{V^2} \times 10^4 = 415$	$\frac{cD^3P}{V^2} \times 10^4 = 407$

c	D	V	$\frac{cD^3}{V^2} \times 10^4$	D	V	$\frac{cD^3}{V^2} \times 10^4$	D	V	$\frac{cD^3}{V^2} \times 10^4$
30	1·850	438	9·90	2·200	506	12·5			
40	1·787	469	10·35	2·123	562	12·1			
50	1·720	506	9·94	2·076	604	12·2			
60	1·687	540	9·90	2·048	642	12·5			
70	1·665	569	10·00	2·015	680	12·3			
80	1·640	594	10·02	1·985	715	12·2			

$P = 39{\cdot}0$	$P = 30{\cdot}1$
$\frac{cD^3P}{V^2} \times 10^4 = 391$	$\frac{cD^3P}{V^2} \times 10^4 = 374$

Table II.—Nitrogen.

c	D	V	$\frac{cD^3}{V^2} \times 10^4$	D	V	$\frac{cD^3}{V^2} \times 10^4$	D	V	$\frac{cD^3}{V^2} \times 10^4$
20	—	—	—	—	—	—	1·066	378	1·69
30	0·743	341	1·05	0·873	375	1·42	0·956	408	1·57
40	0·683	353	1·02	0·818	394	1·41	0·907	432	1·59
50	0·637	368	0·98	0·783	411	1·44	0·857	452	1·55
60	0·613	372	0·99	0·759	428	1·42	0·830	471	1·55

$P = 39{\cdot}1$	$P = 28{\cdot}8$	$P = 24{\cdot}1$
$\frac{cD^3P}{V^2} \times 10^4 = 40{\cdot}0$	$\frac{cD^3P}{V^2} \times 10^4 = 41{\cdot}3$	$\frac{cD^3P}{V^2} \times 10^4 = 38{\cdot}4$

Table II—*continued.*

c.	D.	V.	$\frac{cD^3}{V^2} \times 10^4.$	D.	V.	$\frac{cD^3}{V^2} \times 10^4.$	D.	V.	$\frac{cD^3}{V^2} \times 10^4.$
20	1·236	414	2·19	1·477	475	2·86	1·737	554	3·42
30	1·135	453	2·07	1·382	535	2·76	1·628	617	3·39
40	1·068	486	2·03	1·322	583	2·72	1·553	670	3·34
50	1·025	517	2·01	1·280	615	2·76	1·493	720	3·22
60	1·000	545	2·02	—	—	—	1·473	760	3·34

P = 19·9   P = 15·4   P = 12·9

$\frac{cD^3P}{V^2} \times 10^4 = 40·8$ $\frac{cD^3P}{V^2} \times 10^4 = 42·5$ $\frac{cD^3P}{V^2} \times 10^4 = 42·5$

Table III.—Air.

c.	D.	V.	$\frac{cD^3}{V^2} \times 10^4.$	D.	V.	$\frac{cD^3}{V^2} \times 10^4.$	D.	V.	$\frac{cD^3}{V^2} \times 10^4.$
15	—	—	—	1·050	355	1·38	1·433	423	2·42
20	0·824	342	0·942	0·977	368	1·37	1·335	450	2·35
30	0·733	358	0·920	0·890	392	1·37	1·236	493	2·33
40	0·686	372	0·932	0·825	411	1·33	1·170	533	2·25
60	0·605	396	0·848	0·750	444	1·28	1·100	600	2·22

P = 43·0   P = 30·7   P = 17·3

$\frac{cD^3P}{V^2} \times 10^4 = 39·2$ $\frac{cD^3P}{V^2} \times 10^4 = 41·1$ $\frac{cD^3P}{V^2} \times 10^4 = 39·4$

c.	D.	V.	$\frac{cD^3}{V^2} \times 10^4.$	D.	V.	$\frac{cD^3}{V^2} \times 10^4.$	D.	V.	$\frac{cD^3}{V^2} \times 10^4.$
15	1·805	505	3·46	2·180	590	4·47	2·555	670	5·57
20	1·719	547	3·40	2·090	640	4·45	2·473	742	5·50
30	1·628	612	3·45	1·984	710	4·40	2·352	840	5·53
40	1·560	672	3·36	1·950	810	4·52	2·300	940	5·52
60	1·485	768	3·33	1·900	950	4·56	—	—	—

P = 12·1   P = 9·0   P = 7·2

$\frac{cD^3P}{V^2} \times 10^4 = 41·2$ $\frac{cD^3P}{V^2} \times 10^4 = 40·3$ $\frac{cD^3P}{V^2} \times 10^4 = 39·8$

Table IV.—Oxygen.

c.	D.	V.	$\frac{cD^3}{V^2} \times 10^4$	D.	V.	$\frac{cD^3}{V^2} \times 10^1$	D.	V.	$\frac{cD^3}{V^2} \times 10^4$
15	—	—	—	—	—	—	—	—	—
20	0·790	850	0·803	1·069	385	1·65	1·193	418	1·95
30	—	—	—	0·950	402	1·59	1·071	434	1·96
40	0·625	362	0·749	0·876	418	1·54	1·000	456	1·93
60	0·555	374	0·734	0·784	444	1·46	0·908	491	1·86

P = 52·2	P = 25·0	P = 19·4
$\frac{cD^3P}{V^2} \times 10^4 = 39\cdot6$	$\frac{cD^3P}{V^2} \times 10^4 = 39\cdot1$	$\frac{cD^3P}{V^2} \times 10^4 = 37\cdot3$

c.	D.	V.	$\frac{cD^3}{V^2} \times 10^4$	D.	V.	$\frac{cD^3}{V^2} \times 10^4$	D.	V.	$\frac{cD^3}{V^2} \times 10^4$
15	1·500	439	2·62	1·758	491	3·38	2·306	607	5·02
20	1·407	460	2·63	1·669	525	3·37	2·210	650	5·12
30	1·290	500	2·57	1·550	580	3·33	2·100	730	5·22
40	1·225	536	2·56	1·483	620	3·40	2·025	800	5·19
60	1·140	598	2·49	1·410	700	3·43	1·940	910	5·27

P = 15·0	P = 11·8	P = 7·7
$\frac{cD^3P}{V^2} \times 10^4 = 38\cdot6$	$\frac{cD^3P}{V^2} \times 10^4 = 38\cdot5$	$\frac{cD^3P}{V^2} \times 10^4 = 39\cdot6$

On the Discharge of Negative Electricity from Hot Calcium and from Lime.

By FRANK HORTON, D.Sc., B.A., Fellow of St. John's College, Cambridge.

(Abstract.)

This paper contains an account of some experiments in which the negative leak from hot calcium was compared with that from platinum and from lime under similar conditions. The experiments were conducted in an atmosphere of argon or helium at a few millimetres pressure. The method of experimenting was as follows:—The negative leak from a platinum strip, heated by an electric current, was first investigated. The temperature of the strip was indicated by a thermo-couple of wires of platinum and platinum with 10 per cent. of rhodium, and the leak was measured by a delicate d'Arsonval galvanometer. Without changing the apparatus, the cathode was covered with metallic calcium by sublimation from an electrically heated calcium wire situated in the discharge tube near to the cathode. The negative leak from the calcium-covered cathode was determined at different temperatures. Some pure oxygen was then let into the apparatus and the calcium on the cathode was oxidised to lime. The excess of oxygen was then removed and the negative leak again measured. Finally, hydrogen was let into the apparatus and the effect of this gas on the negative leak from lime was investigated.

The results contained in the paper may be summarised as follows:—

(1) The experiments with a platinum cathode showed that the negative leak from platinum in helium or argon at low pressures is practically the same as in air or oxygen. The variation of the negative leak per square centimetre with the temperature of the cathode can be expressed by an equation of the form used by O. W. Richardson and by H. A. Wilson, viz., $x = A\theta^{\frac{1}{2}}\epsilon^{-Q/\theta}$, where x is the current in ampères, θ the absolute temperature, and Q and A are constants.

(2) The negative leak from calcium is much greater than from platinum at the same temperature. As with platinum, the variation of the leak with temperature can be expressed by the above equation, but the values of the negative leaks from calcium at different temperatures do not so closely agree with the values calculated from the equation as in the case of platinum. This is probably due to the greater experimental difficulties attending the use of calcium.

(3) On oxidising the calcium on the cathode to lime there is an enormous increase in the negative leak, the leak from a lime cathode at 950° C. being about the same as the leak from calcium at 1400° C. The variation of the negative leak from lime with the temperature is not constant, but slowly decreases with continued heating.

(4) The negative leak from lime in hydrogen is much greater than that in air or helium.

Since calcium is a much more electro-positive metal than platinum, it was to be expected that the negative leak from calcium would be greater than that from platinum at the same temperature. It would also be expected that the negative leak from calcium would be greater than that from lime under similar conditions; for in the case of lime we should expect the presence in the molecule of the electro-negative atom of oxygen to act as an attracting force tending to retain the escaping corpuscle. The present experiments, however, show that the negative leak from lime is greater than that from calcium. It is interesting to note that the metallic oxides which give the largest emissions of negative corpuscles when heated are the alkaline earths, and it is these also which exhibit most strongly the property of glowing when heated to a high temperature. It is not improbable that there is some connection between these two phenomena.

Experiments on the Dark Space in Vacuum Tubes.

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

1. When an induction spark passes through an exhausted vacuum tube we see, firstly, a luminous layer coating the cathode, next a dark space ; beyond the outer edge of this dark space comes a luminous envelope, then another blank, sometimes called "Faraday's dark space," and, lastly, the positive column. Between the second dark space and the positive column, if the exhaustion is suitable, stratifications occur. In the present paper I speak of the first dark space extending from the luminous layer on the cathode to a more or less sharply defined luminous boundary. The luminous coating on the cathode is produced by the ionisation of the atoms of residual gas and the union of the electrons from the metal with the positive ions, with liberation of a further jet of electrons* starting from the neighbourhood of the cathode with velocities of the order of that of light.

2. The dark space is a measure of the mean free path of the electrons, and its outer luminous margin is the scene of the collisions between free electrons and the column of positive ions. It varies in size with the degree of exhaustion. At a pressure of about 4 mm. it begins to appear as a narrow space, a fraction of a millimetre removed from the negative pole, and grows larger as the exhaustion increases. At a pressure of about 3 mm. the margin of the dark space is about 4 mm. from the negative pole. At an exhaustion of 0·25 mm. it is about the best size for such work as I now describe. When the exhaustion is pushed further, the outer boundary becomes indistinct and soon fades away, the dark space now filling the tube, the walls of which glow with a phosphorescent light. It is to the phenomena occurring within this dark space that I have devoted years of work, and I now have the honour of presenting to the Society some account of the results of my prolonged investigations; in parts they lead to conclusions which have been already made public by other observers.

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* Not long before his death, Sir George Stokes proposed to me to adopt a systematic nomenclature in this branch of research, and suggested the following :—

"RAY—A disturbance propagated in the ether.

JET—A discharge of electrons.

EMANATION—To include both Rays and Jets."

(The term *Emanation* is now appropriated to Rutherford's radio-active gas.)

"A cathode *jet* of electrons impinges on a metal and causes it to emit (X) *rays*. A self-luminous *emanation* from a radium-barium salt consists of *rays* of light and *jets* of electrons."

3. Fifteen years ago* I delivered an Address in which I described experiments undertaken to see how the positive and negative charges were distributed in vacuum tubes carrying a high tension current. At that time the electron theory was unknown, and my descriptions were given in the language then in use. What I then spoke of as " a stream from the negative pole," " negative molecules," " negative atoms projected violently from the negative pole," " ultra-gaseous state of matter," " radiant matter," etc., may now be included in the term "electrons." As the experiments I more particularly wish to bring before the Society arise out of my antecedent work, I will briefly describe some which are necessary to the proper understanding of the subject, merely translating into modern terms language which now has become archaic.

It is my hope that the experiments here described may be worthy of record as illustrating or testing the principles of the quantitative theories that have been elaborated to represent the phenomena.†

The Dark Space at Pressures down to 0·1 *mm.*

4. I had been examining the electrical condition of the interior of a vacuum tube carrying an induced current, by means of idle poles passing through the glass at different points.

A tube was made as shown in fig. 1. A is the negative pole, constructed so that it can slide to and fro along the narrowed axis of the tube by tapping the end, metallic contact being maintained by means of a fixed and movable
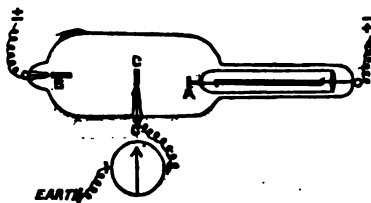
Fig. 1.

sliding wire, as shown; B is the positive pole; C is an idle pole. A and C are flat discs of aluminium, B is a short piece of aluminium rod. In these experiments C was connected to earth through a reflecting galvanometer‡ D E.

* 'Journal of the Proceedings of Electrical Engineers,' Part 91, vol. 20.

† *Cf.* J. J. Thomson, ' Conduction of Electricity through Gases,' 2nd ed., 1906.

‡ The galvanometer shown is merely diagrammatic. In these and the following experiments several different instruments were used, according to the sensitiveness required—low resistance needle, high resistance reflecting galvanometers, and Lippmann's electrometer.

The adjustable pole was put so that the idle pole was exactly halfway between the poles A and B. These were connected with the two poles of an induction coil, the break being unscrewed so that it would not act, and contact being made by hand. The tube was attached to the pump, but at first was not exhausted, my object being to see what effect differences of pressure had on the direction and intensity of the current passing from the idle pole to earth.

One contact of the coil was made by hand, sending one spark through the tube, A being the negative pole. No movement of the needle was seen. The coil commutator was reversed, making B negative, and another spark was sent through. No current passed to earth.

5. Exhaustion now proceeded, a spark being passed at intervals as the mercury gauge rose, but nothing was seen on the galvanometer until the pressure sank to 14·5 mm., when, in making contact, a faint jerk of the spot of light was noticed when terminal A was made anode, but none when it was cathode. At 13 mm. the same faint movement was observed, only a little stronger when A was anode, but none when A was cathode. At 12 mm., A being anode, the spot of light moved in the negative direction 36°, at 10 mm. it moved 34°, and at 7·5 mm. it moved 33°. Here for the first time, on making A the cathode, the galvanometer deflection was 17° in the positive direction. Observations were continued at intervals as the exhaustion rose, the deflection being + or − as the direction of the secondary current through the tube was reversed, and it continued to give positive and negative deflections down to a pressure of 0·0001 mm., when a current was still found to pass. These results are plotted on the diagram (fig. 2). Using
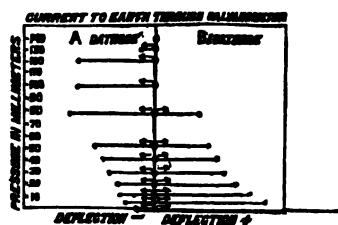
Fig. 2.

a Lippmann's electrometer instead of a reflecting galvanometer, I could detect + and − movements at considerably higher pressures than 14·5 mm.

Effect of Size of Tube on the Dark Space.

6. Does the size and does the shape of the tube in which the dark space is formed modify its appearance? By way of test I made an apparatus,

shown in fig. 3. The poles in A and C are of the same size, and are the same distance apart. The poles in B are cylindrical wires and are closer
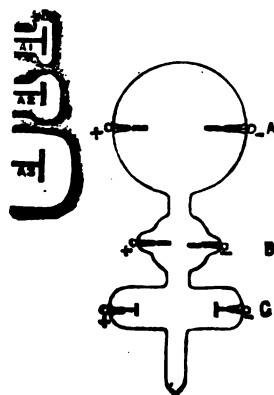
Fig. 3.

together. In this experiment the induction current was passed separately through each section of the apparatus.

A pressure was obtained so that the dark space in A was about 2 mm. from the face of the pole, as shown in A_1. On connecting the wires successively to B and C, there is very little difference in the appearance of their dark spaces, which resemble A_1. At a slightly higher exhaustion the dark spaces are as in A_2 in all three tubes, but the glass of the cylindrical tube, C, is much more phosphorescent than the others. On further exhausting, a considerable difference has come over the tubes. The dark space in A is well defined, and extends two-thirds the distance between the poles, as in A_3. In B the boundary cannot be seen, and the glass is slightly phosphorescent. The tube C appears to be almost free from gas or foggy appearance, and the whole tube glows with a bright green phosphorescent light.

Connecting the poles to the induction coil in parallel, so that the current passes simultaneously through the three, the sequence of phenomena is similar to that already described.

It therefore appears that the size of the enclosing tube does not influence the size of the dark space so long as this is to be seen, but as exhaustion proceeds the dark space is seen for a longer time and becomes of a larger size in a large tube, while with a small tube the dark space disappears when it gets near the wall, and the phosphorescence of the glass appears. I have already shown that the power of inducing phosphorescence seems to be at its maximum where the electrons and positive ions are in the act of

reuniting. Yttria and other phosphorescent bodies glow best at the edge of the dark space, and when the dark space extends to the sides of the tube the electrons unite with its positive ionic lining, and thereby cause the glass to phosphoresce.

Electrical Conditions about the Dark Space.

7. At the highest vacuum (0·0001 mm.), the tube being almost non-conducting, when I connected the idle pole with a delicate electrometer it always showed positive electrification, in spite of the idle pole receiving the full impact of the electrons shot from the negative pole, and for a long time I could get no indications of any negative charge inside the tube. Occasionally, when the vacuum was very high, I detected negative electrification; the following piece of apparatus was devised whereby this point could be investigated more closely.

8. Figs. 4, 5, and 6 show different phases of the same tube. The tube is cylindrical, and is furnished with three poles, A, B, and C. A and B are the
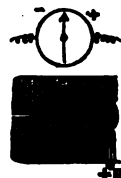
Fig. 4.   Fig. 5.   Fig. 6.

terminals, and C is an idle pole, capable of being moved along the axis of the tube by tapping the end, metallic contact being maintained by means of a fixed and movable sliding wire, as shown. The negative pole A is flat, and the positive pole ring-shaped; the idle pole C is also flat. The tube was exhausted to a pressure of 0·25 mm., at which point the dark space round the negative pole had the appearance shown in fig. 4. The idle pole C was then brought by tapping to a position well within the dark space, and it was connected to earth through a galvanometer. The indications showed that a strong negative current was passing from C to earth.

9. The idle pole was then brought to a position well outside the dark space, as shown in fig. 5. The galvanometer now indicated a positive current flowing from C to earth.

10. Tapping was continued, and the idle pole was gradually brought nearer to the negative pole. The indication of the galvanometer gradually became less, until, on reaching the dark space (as shown in fig. 6), no current was shown on the galvanometer.

11. Another tube (shown in figs. 7, 8, and 9) was made, having two fixed idle poles, C and D, A (—) and B (+) being the poles connected to the induction coil. Pole A was made movable like the idle pole in the former instance, and the tube was exhausted to 0·25 mm., when the dark space surrounding the negative pole was well defined. At first the movable — pole was so placed that the idle pole C was well inside the dark space,
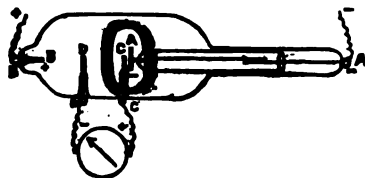
Fig. 7.   Fig. 8.   Fig. 9.

and the idle pole D outside it, as shown in fig. 7. On connecting the idle poles D and C through a galvanometer, the needle showed that a current passed in the direction that would be produced if C were zinc and D copper of a copper-zinc couple. An electroscope showed that each idle pole was charged positively.

12. The negative pole A was next placed in the position shown at fig. 8, so that both idle poles were outside the dark space. The galvanometer now showed that a current passed through it in the same direction as if C were copper and D zinc.

13. Finally, when the negative pole was still further removed, as shown in fig. 9, a point was found where no definite deflection could be obtained on the galvanometer, the needle oscillating irregularly a degree or two on each side of zero. This occurred when the pole A was in such a position that the outer border of the dark space just reached to the pole C. The electroscope still showed both poles to be positively electrified.

14. A tube was made as shown in fig. 10. The terminals of the tube are shown at A and B. B is the positive pole, consisting of a short thick piece
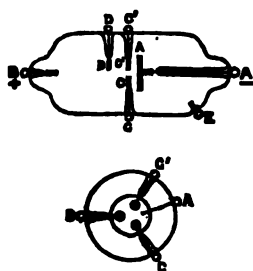
Fig. 10.

of aluminium wire. The negative pole A consists of a flat plate of aluminium, supported near the middle of the bulb on a wire guarded in a glass tube. C and C' are small flat aluminium discs, 3 mm. in diameter, held at the ends of guarded metal wires on the same level and 3 mm. from the negative pole. D is a similar pole, 6 mm. further from the negative pole. These three idle poles were so placed that they were not in each other's way, a clear space being between each and the negative pole. Seen in plan, their positions were as shown at the side (fig. 10).

The tube was exhausted till the dark space round the negative pole extended beyond and well enclosed the two poles C and C'. On connecting them through a sensitive galvanometer while the current was passing between A and B, no appreciable current was detected.

15. C and C' were now joined by an outside wire, so as to make one pole of them. They were connected with the galvanometer, and pole D was joined to the other side of the galvanometer.

Air was let in and exhaustion was continued till the dark space was about 2 mm. from the negative pole, as in fig. 11. The galvanometer showed that a current passed as if C C' were copper and D zinc, giving a deflection of +186° (arbitrary scale).

FIG. 11.   FIG. 12.   FIG. 13.

A little further exhaustion slightly increased the size of the dark space, and the deflection of the galvanometer sank to +86°. A few more drops of mercury passed through the pump brought the deflection down to +60°. The dark space now was beginning to enclose the two poles C C'. A few more drops of mercury passed, and the galvanometer showed only a slight flicker, a degree or two one side and the other of zero, the appearance being as in fig. 12. At a slightly higher exhaustion the deflection became negative, —62°. Exhaustion was continued until the outer edge of the dark space commenced to touch the idle pole D (as in fig. 13), when the galvanometer deflection was —196°, as if C C' now were zinc and D copper. The vacuum was pushed a little further, and the deflection became —133°. A little further it dropped to —86°, the dark space becoming large and indistinct, seeming to fill the bulb, and the green phosphorescence of the glass also becoming apparent. At a higher exhaustion the deflection was again zero, and on pushing the vacuum till the whole bulb glowed green, a steady current of +155° was shown in the opposite direction. At the highest

exhaustion I here obtained, the bulb being almost non-conducting, no current passed through the galvanometer.

16. Another pole, E, was now added to the tube below the negative A (fig. 10), and the experiments were repeated, using A (—) and E (+) as the poles for the induction current. The galvanometer deflection was taken between the idle poles C C' and D. I thought it probable that the positive ions in the last experiment, beating in a stream from B to the idle poles, might have complicated the observations of current direction, hence the pole B was not used. The appearance of the dark space was practically the same at the different exhaustions as it was in the previous instance, and the deflections of the galvanometer were successively as follows:—20°+, 25°+, 22°+, 0°, 200°—, 130°—, 200°—. Here the green phosphorescence of the tube commenced to appear. 20°— ; at this degree of exhaustion the tube was almost non-conducting.

Relation between Pressure and Current in Dark Space.

17. I sought to ascertain the pressure at which the change from positive to negative took place, and the appearance of the dark space on one side and the other of the critical pressure.

A "dark space" tube was made as shown in fig. 14, and was sealed on to the pump by the side of the working tube (fig. 10) in which the experiments were tried. This "dark space" tube was used solely as an indicator of the changes in the appearance of the dark space when the galvanometer indications were taken during the experiments in the working bulb. A
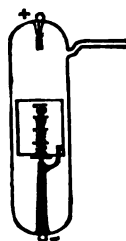
FIG. 14.
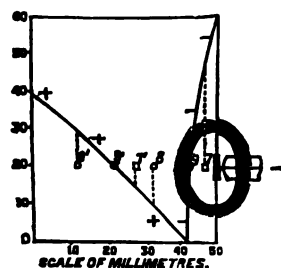
FIG. 15.

mica scale, divided into millimetres, was fixed across the centre of the negative pole, so as to enable measurements of the dark space to be obtained. By means of this tube, exhausted simultaneously with the working tube and actuated with the same induction coil, the distance of 2·5 mm. from the outer edge of the dark space to the flat pole was verified. It was noticed that when close to the critical pressure, but with a slight positive current, the

edge of the dark space was fairly sharp, but that when the change in deflection took place it was accompanied by a loss of sharpness of the outer boundary.

The radius of the dark space in this particular tube (fig. 10) was 2·5 mm., but with the idle pole C further from the negative pole the dark space would have to be larger to reach it, and the critical pressure would have to be a little higher.

The result of a ceaseless series of experiments with many kinds of vacuum tubes, and galvanometers and electroscopes of varying sensitiveness, is that the direction of the current between the two idle poles C and D changes as one of them gradually comes into the dark space. The following explanation appears to me reasonable, and to account for all the facts hitherto observed.

18. In fig. 15 I show diagrammatically in the form of curves the distribution of the negative and positive potential in the interior of the vacuum tube during the experiments illustrated in figs. 7, 8, and 9. The negative pole and dark space are shown at the right. The steep curve on the right represents negative and the curve on the left positive potential. The excess of electrons extends only to the edge of the dark space, the rest of the tube being positively charged.

The square dots marked 7 7' show the position of the idle poles in fig. 7, where one pole is well within the dark space and the other outside it. It will be seen that pole 7 has a strong negative potential and pole 7' a positive potential. In this case a current flows through the galvanometer connecting 7 and 7', in the same direction as it would were 7 zinc and 7' copper.

In the next position the idle poles are represented by hollow dots, 8 and 8', as in fig. 8, where both poles are well outside the dark space; a current flows through the galvanometer as if 8 were copper and 8' zinc.

Finally the solid dots 9 9' show the positions of the idle poles in fig. 9, where one pole is on the edge of the dark space and the other outside. Here, therefore, the galvanometer shows no current.

Action of the Walls of a Vacuum Tube.

19. In studying the movements of the electrons in the dark space, it must be borne in mind that the distance of the walls of the vacuum tube from the cathode materially influences the appearance of the luminous phenomena in the interior.

To show the force of this influence, I sealed in tube, fig. 16, two exactly similar phosphorescent screens, C and D. At one end of each screen is a mica gate, E E', to stop all phosphorescent action except in the centre of the screen. A flat pole faces each A A' gate. Another pole is at B. C is one of the

screens in the narrow part of the tube, and therefore close to the walls. The other screen, D, is in the spherical portion, and therefore far removed from the walls. The poles A and A' are connected and made negative poles, the pole B being the positive. On passing the current at a pressure of 0·001 mm., the electrons stream with a very high velocity from the two negative poles and produce phosphorescent effects. The screen D, in the globular part,
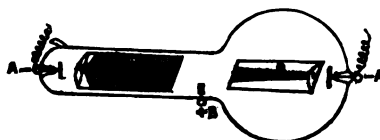
Fig. 16.

shows a narrow sharp streak of light, proving that here the electrons are free to follow their normal course straight from the pole, with no appreciable interference till they strike the screen. In the cylindrical part of the tube, however, the positive ions on the inner side of the glass drag the electrons from their normal course, with the result that the stream widens out sufficiently to cause nearly the whole surface of the screen C to glow with a uniform subdued phosphorescent light.

Dark Space Phenomena at the Lowest Attainable Pressures.

20. In a U-shaped vacuum tube at a moderately high exhaustion the stream of phosphorescent light marking the path of the electrons stops abruptly at the bend, and no appearance of turning round the corner or of reflection from the surfaces of the bend can be detected.

In a vacuum approaching the non-conducting stage, some of the electrons succeed in turning the corner somewhat by reflection, or produce by collisions others which do so, and pass a considerable distance along the further limb of the tube. These stray streams are still able to produce phosphorescence when falling on glass, sulphide of calcium, or yttria.

I have tried many ways of detecting the presence of these wandering electrons, and in the experiments now to be described I used photography to aid in their detection.

Photography inside the Vacuum Tube.

21. A photographic film exposed to the emanations inside a vacuum tube is strongly affected. Here we have positive ions, electrons, and Röntgen rays acting together, and I endeavoured to differentiate the effects of these three streams, analogous to the α, β, and γ rays of radio-active substances.

Experiments were instituted at first to see if the electrons which had lost much of their original velocity would affect a photographic film when it was out of the line of fire.

A U-shaped tube was made, as shown in fig. 17, A being the negative pole and B the positive.   At the further end a flat plate of glass is cemented
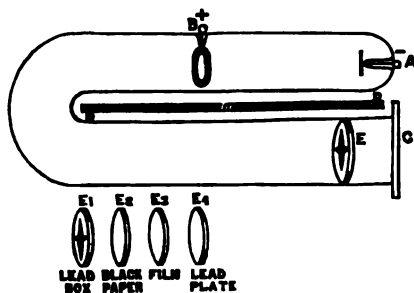
Fig. 17.

on.   E is a lead box containing a photographic film, built up in the following manner :—The lead is 0·5 mm. thick, and the finished box is 20 mm. diameter. E_1 is a disc of lead, 2 mm. larger in diameter than the finished box, and having a star cut out of the centre.   A disc of black paper, E_2, is put next the star disc, and a photographic film, E_3, is put next to the paper, the sensitive side of the film facing the star. E_4 is a plain disc of lead acting as a backing to the sensitive film.   The whole put together in the above order, the edges of the front disc of lead are turned over the back. The lead box so packed is put into the further arm of the tube (which may be called the *laboratory* end) in an upright position, as shown, the stencil star facing the bend of the tube.   A thick plate of brass is interposed at D D' to cut off any Röntgen rays which might otherwise fall on the sensitive film.

The tube was well exhausted and carefully heated, but not to a sufficiently high temperature to injure the sensitive film.   When the sound of the pump showed that the vacuum was high, the current was turned on for a minute. Gas was immediately given off, and the operations of exhausting and passing the current were repeated many times till a high vacuum was produced, the glass phosphorescing a bright green.   The current was then kept on for 30 minutes, the pump working occasionally to prevent the vacuum deteriorating.   When finished, and air let in, the lead box was removed by the window C.

On development, a good image of the star was seen, the rest of the film being unaffected.

22. The experiment was repeated, using a disc of aluminium-foil 0·2 mm. thick instead of the black paper E₂. After a high vacuum was reached, the current was kept on, as before, for half an hour. On development, a good image of the star was seen.

23. At a very high exhaustion in a darkened room, green phosphorescence of the glass can be detected to the end of the laboratory limb of tube. At the further end the action is very faint and difficult to see. Still the experiment proves that electrons in diminished numbers can get so far. I imagine that the velocity of impact which will produce phosphorescence of glass will also generate Röntgen rays when the electrons are suddenly arrested. A photographic film facing the bend of the tube and backed with metal is darkened by the rays, and I now sought to ascertain if a similarly disposed film at the further end of the film-holder would be also affected.

24. This experiment was repeated, using, as before, an aluminium disc behind the lead star, but the box was turned round so that the star and sensitive surface of the film faced the glass window C instead of facing the bend in the tube. The current was maintained for four hours and the pump kept going so as to keep the vacuum very high. At the lowest pressure at which the current would pass, a concentration of mobile green phosphorescent light appeared on the inner surface of the laboratory limb of the tube, a little before the place where the lead box stood. From the shape and appearance of the green patch of light it looked like a reflection of rays from the sides and curved part of the other limb of the tube. The patch was very sensitive to the approach of fingers, being driven sideways when a finger was within 3 inches of the glass. A cold metal rod held in the hand had the same effect, and a strong permanent magnet a similar action, but no stronger than the finger.

After four hours' exposure, the sensitive film was removed and developed. No image of the star was to be seen, but strong black patches at the edges of the film showed that an action had there taken place, apparently by leakage of electrons between the folds of the lead.

25. A larger box film-holder was made of brass, 2 mm. thick and 22 mm. external and 18 mm. internal diameter. Five small holes were drilled through the bottom of the box, and the brass back was accurately fitted so as to leave an internal space for the discs of film, aluminium, paper, etc. It was then packed as before. The first experiment was to try if the emanations would penetrate a thicker piece of aluminium-foil than was formerly used. (In the former case the foil was 0·2 mm., in the present case 0·5 mm. thick.) The box was put into the laboratory limb with the

film side facing the stream. After the tube was well exhausted the pump and current were kept going for two hours, a high vacuum being maintained all the time. On development, the film showed a good image of the five holes. The aluminium screen also was darkened under each hole in the brass.

26. Another similar experiment was tried with the same apparatus, the brass film-holder being packed, first with a thin piece of microscopic cover glass next the holes, then an aluminium-foil screen 0·5 mm. thick, then the sensitive film facing the aluminium and glass; finally the back cover was put on. The box was put in the laboratory limb with the poles facing the bend in the tube. The tube was exhausted and the current passed as before and kept going for three hours. On opening the box there was no visible discoloration of the glass film next the holes, but an image of the spots could be brought out temporarily by breathing on the surface. Nothing was seen on the aluminium film. On development, a good image of the spots was seen, and there was a little irregular darkening round the edge, occasioned probably by light conducted into the box by the glass circle.

27. It is fair to assume that the emanations I am dealing with in the laboratory limb of the U-tube consist of electrons whose velocity has been greatly diminished by collisions with atoms of matter. Besides these slow-moving electrons there must be Röntgen rays, for at the bend of the tubes bright green phosphorescence is seen on the glass—not only in the direct line from the negative pole, but a little further round the corner. The electrons suddenly arrested at the bend of the tube will also generate Röntgen rays, and some of these will be able to affect the film and penetrate an aluminium screen. Any positive atoms which may be liberated near the metal film-holder will be absorbed by the covering aluminium window.

Penetrating Power of the Rays or Jets.

28. The following experiment was tried to ascertain the penetrating power of the emanations affecting the sensitive film.

Thirteen discs of sensitive film were packed in a brass box, A, fig. 18, closed at one end, and at the other end a lead lid (shown at B), in the centre of which was cut a cross. Between the lead cross and the first disc of sensitive film a disc of aluminium (0·2 mm. thick) was interposed; all the films had their sensitive surfaces facing the cross. The packed box was put in the laboratory limb of the U-tube, the cross facing the bend, and the whole was exhausted to a high point, occasionally passing the current for a short time to drive off occluded gas. When the tube showed good phosphorescence the current was kept on for one hour, the pump being worked occasionally so as to keep the vacuum a little short of non-conducting.

On development, the image of the cross could be seen on the seven discs nearest to the bend of the tube, no action having taken place on the other six. The intensities of impression diminished from the first to the seventh.
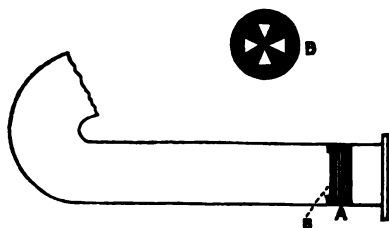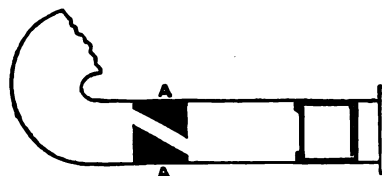
FIG. 18.   FIG. 19.

29. On examining the U-tube it was seen that if Röntgen rays were the cause of the action, they must have come from a part of the bend much out of the direct line of fire from the negative pole. But I have said that the glass phosphoresced right round the bend, and a part of this phosphorescing glass might be in a direct line with the box of films. I therefore devised a piece of apparatus which would probably settle the point as to the origin of these acting rays. The figure (fig. 19) shows the laboratory limb of the tube. A thick cylinder of type metal, A A (19 mm. long) is fitted into the tube in front of the film-holder, and through it is drilled a diagonal hole 7 mm. diameter. The film-holder is a brass cylinder 20 mm. long, closed at the further end, and in front having a thick lead cover with a 3-mm. hole through the centre, and a window of aluminium 0·2 mm. thick close behind it. Close to the aluminium is a sensitive film, and at the further end of the cylinder another sensitive film is fixed, a space of about 19 mm. separating the two. When the limb of the tube is packed ready for exhaustion, it is evident that no rays projected in straight lines from any part of the bent part of the tube can find their way through the diagonal hole and the aluminium window in the lead cover of the film-holder.

The pump was kept at work for some hours, with an occasional passage of the current, until the vacuum was at a high point, and non-conduction was commencing. In the dark the green phosphorescence of the glass could be traced completely round the bend and up to the thick metal plug, where it ended abruptly. At the bend a good image of the ring positive pole was seen on the glass, and, also, there was a sharp outline of the edge of the active arm of the tube. A careful examination of the different parts of the tube was made for Röntgen rays. These were seen issuing from all parts of the tube where the phosphorescence was full, and they could be detected coming also from the surface of the metal block facing the bend. Very faint indications

of Röntgen rays could be detected, also, coming from the lead and aluminium screens in front of the sensitive films in the laboratory end.

The current was passed and the pump kept going for 4¼ hours, during which time the tube was in its most active state. On removing the films and developing, no image whatever could be seen on either of them; they were quite clear and uninfluenced.

These experiments point to the conclusion that the emanations which act on the sensitive film are Röntgen rays emitted from the bend of the tube out of the direct line of fire from the negative pole. During the progress of the last experiment with the U-shaped tube, when the vacuum was high and the phosphorescence of the glass round the bend good, the shadow of the ring pole was seen, and the centre, where the direct jet of electrons from the negative fell, was hot and almost non-phosphorescent.

30. A narrow strip of sensitive film, safely enclosed in opaque black paper, was bent along the outside bend of the tube and held in place with string. It was exposed to the action for 10 minutes, then removed and developed. There was action over all parts, but the densest corresponded to the part inside the shadow of the ring pole.

Thus it appears that active emanations come from parts of the tube not in the direct line of fire from the negative pole, and experiments show that it is probable these are Röntgen rays, and if so, the rays will not diverge from a straight line when once started on their course, while jets of electrons with much diminished velocity will spread sideways. This is shown in the following experiment, which also illustrates the penetrating powers of the rays. The same U-tube was used as in previous experiments, but the film box was altered.

Röntgen Rays from Secondary Streams of Electrons.

31. A thick lead screen (fig. 20) was divided along its diameter so as to form two half discs, A and A'. These discs were put 5 mm. apart in front of the brass holder, and turned so as to expose a V-shaped opening, as shown. Next to the inner half disc is a disc, B, of aluminium 0·2 mm. thick, and close behind come five sensitive films, C. A space of 2 mm. now intervenes, and then come five more films, D, close to the back of the box. The films all face the bend of the tube, the box being near the window end. After good exhaustion the current was kept on for one and a-half hours, and on development an image of the V-shaped opening was seen on all 10 films. The parts of the film not exposed to the direct rays passing through the V aperture remained quite unaffected, showing that stray electrons had not turned round the edge of either half disc of lead. Careful examination

showed (1) that the intensity of the impression decreased as the rays had more and more films to penetrate; (2) that the image to a slight degree was multiple, showing that the rays did not come from a point, but from several adjacent parts of the bend of the tube; (3) that the 10 images were not of the same size, showing that the rays had appreciably diverged when passing through the films.

FIG. 20.
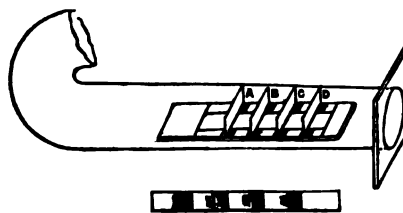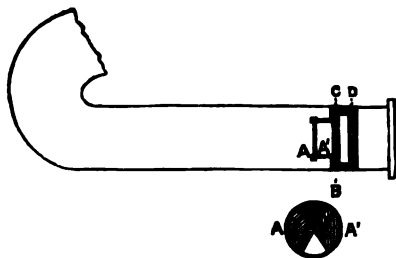
FIG. 21.

32. I wished to ascertain (1) if the emanations acted on the sensitive film when the face was not pointing towards the bend, and (2) if the action fell off as the distance from the bend increased. One of the experiments illustrated in fig. 17 shows that action does not take place when the sensitive film is turned facing the end of the laboratory limb, and having lead and aluminium obstructions guarding it; but something more was wanted before the action could be quite understood. A box of assay lead, 0·15 mm. thick, was made, 100 mm. long and 10 mm. wide, to hold the sensitive film, the aluminium-foil, and the lead screens. At one end a lead cap slipped on so as to keep the contents light-tight. Holes were cut through the upper layer of lead, in the form of a cross and five rectangles. A strip of sensitive film was first put in, then a strip of aluminium-foil 0·2 mm. thickness was put over it, and then came the upper surface of the box with holes as described. The box as packed was put into the laboratory end of the U-shaped tube, and a good exhaustion obtained. When the glass phosphoresced well the current was kept going for two hours. On removing the film and developing it, images of the six holes were seen. The impression at the end nearest the bend was the strongest, and the intensities of the other images gradually diminished towards the other end, the image of the last hole being extremely faint.

33. The greater part of the front of the lead box was now cut away, leaving a rectangular opening exposing most of the aluminium-foil beneath. Four upright pieces of lead-foil were placed equidistant along the opening, bridging it across and leaving square openings, A, B, C, D, separated by lead screens (as in fig. 21). A strip of sensitive film was first slipped in the

box, and in front of it was put an aluminium plate 0·2 mm. thick. The box was laid in the laboratory end of the U-tube, and after good exhaustion the current was passed for two hours. On development, an impression was seen beneath each square opening, as shown in the figure, getting fainter as the distance from the bend of the tube increased. It also was noticed that the impression in each square was not uniform in density, but fainter at the side further from the lead upright, and getting denser towards the lead upright. The effect was exactly as if emanations from the bend of the tube had struck each lead upright on the face, and then had been reflected back on to the film, passing through the aluminium screen. The explanation is obvious. Electrons have passed round the bend into the laboratory tube and, striking the face of each lead upright, have there generated Röntgen rays. These rays, not being intense enough to pass through the lead, have affected the sensitive film in front of the screen, the action being strongest at those parts of the film nearest the upright.

34. If this is the explanation, then the substitution of a thin sheet of aluminium for lead in one of the uprights would also generate Röntgen rays, but the rays would get through the aluminium and affect the film on both sides (40). By way of test the first two uprights of lead were removed and replaced by a square of aluminium 0·05 mm. thick, the rest of the packing being as before. After good exhaustion and exposure to the current for two hours at a very low pressure the film was removed and developed. The appearance confirmed anticipation. The film on each side of the aluminium-foil was darkened, as if the acting rays had emanated from both sides of the foil, whilst the appearance round the lead uprights remained as before. These experiments seem to prove that the action is one of Röntgen rays, that electrons which have lost much of their velocity still can generate these rays when they strike lead or aluminium, and also that rays so generated will not pass through lead-foil 0·15 mm. thick, but will penetrate aluminium foil 0·05 mm. thick.

Röntgen Rays from Phosphorescing Yttria.

35. In the experiments so far carried out the body emitting electrons has been the cathode, and the action on the photographic film appears to be due to the generation of Röntgen rays by the sudden arrest of electrons by a solid target, and the penetration of the screen in front of the film by these rays. It became of interest to see if a highly phosphorescent substance would emit Röntgen rays while it was phosphorescing. Ignited yttrium sulphate was now chosen as a target, and the experiment was conducted in the following manner :—

A brass chamber was made, 10 mm. long and 5 mm. wide (as shown at A, fig. 22), consisting of two cylinders fitting tightly one in the other. The
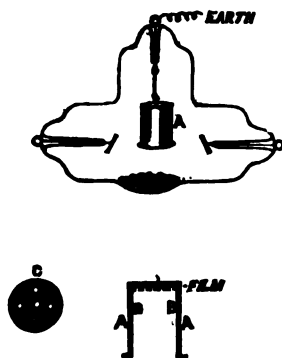
FIG. 22.

outer cylinder, A, is closed at the top, and the inner cylinder, B, is also closed at the top with a disc of brass, C, perforated with five holes. Removing the inner cylinder, a thick disc of lead is first pressed into it to form a bed for the back of the sensitive film; next comes a disc of sensitive film; on this is put a disc of aluminium 0·05 mm. thick—lastly, the inner cylinder is pushed home. The whole is suspended in a vacuum tube as shown, and connected to "earth" by a wire passing through the glass. The cylinder is suspended out of the direct line of fire from either pole, so that the phosphorescent rays from the yttria are the only ones that can get into the cylinder and shine on the perforated cover. Preliminary experiments having shown that the brass cylinder was liable to get very hot, and so injure the film, the outside of the tube was covered with blotting-paper, and a stream of cold water trickled over it throughout the experiment. When the vacuum was good and gas ceased to be liberated on passing the current, the latter was kept on for two hours, the current being alternating, so that each pole was cathode for half the time. On opening the tube and developing the film, a good image of the five holes was seen— a proof that the emanations from the yttria, during the act of phosphorescence, are also accompanied by rays capable of passing through thin aluminium and impressing themselves on a photographic film.

36. It is pretty evident from the results of the foregoing experiments that in the laboratory limb of the U-tube, far removed from the direct line of cathode stream, emanations are present which act on a photographic film, and that these emanations are of the nature of Röntgen rays generated in the neighbourhood of the bend in the tube. The following experiments were instituted to ascertain more definitely the nature of the emanations in

question, and also to see what happens when an aluminium plate is interposed in the line of direct radiations from a flat cathode instead of to the wandering electrons, as in previous experiments.

37. A vacuum tube was made with a flat aluminium cathode and a straight wire anode, as shown in fig. 23. The tube contains a cylindrical brass box, C C D D, closed at one end with a sheet of aluminium, C C, 0·05 mm. thick,
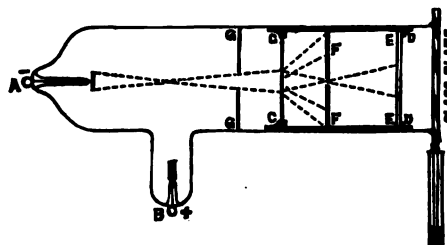
Fig. 23.

and at the other end by a thick plate of brass, D D, in front of which could be put a sensitive film, E E. Inside the box, and 20 mm. from the aluminium plate, C C, is a brass diaphragm having in the middle a 2-mm. hole. In the vacuum tube, 15 mm. from the outside of the box, is fixed a similar brass diaphragm, with a 2-mm. central hole.

A preliminary experiment before placing the diaphragm, F F, in position showed that the narrow jet of electrons passed through the hole in G G, and falling on the aluminium screen, C C, gave rise to emanations that darkened the sensitive film at E E uniformly over the whole surface. Thus, the emanation inside the box is no longer of the character of a jet of electrons, but proceeds in all directions from the surface of the aluminium disc. If, therefore, the diaphragm, F F, is put in position, as shown, it will limit the emanations which affect the sensitive film to a central circle about 8 mm. in diameter. The experiment was tried, a sensitive film being put in its place at E E. After good exhaustion the current was passed for two hours, the pump kept at work, and the vacuum being a little short of non-conducting.

The film, on development, showed a dark disc about 8 mm. diameter in the centre. Outside the edge of the darkened part was a wide space unacted on, showing that the emanation from the pole A, passing through the aluminium disc and the hole in F F, had pursued a nearly parallel direction.

Magnetic Deflection of Part of the Emanations.

38. The dark spot may have been caused by electrons from A or by Röntgen rays. It is not likely to have been caused by the positive ions, as these are arrested by aluminium much thinner than the 0·05 of a mm.

These two agents can easily be differentiated by a magnet. A preliminary experiment was tried to see how much magnetic deflection could be obtained, and whether it was sufficient to detect easily by photography. The apparatus shown in the last figure (fig. 23) was used. The aluminium disc, C C, was removed, the pierced diaphragms, G G, F F, were retained, the end D of the box was removed, and the photographic film in the last experiment was replaced by a phosphorescent screen. The tube was closed and, after exhausting for an hour, the current turned on. A central spot of phosphorescent light was seen on the screen. A magnet below the tube, in the position shown, pulled down the spot about 15 mm. At higher exhaustions the action of the magnet on the emanations was not so strong, but at the highest vacuum at which the current would pass they were appreciably deflected. The magnet was now adjusted so that at a high exhaustion the spot of light was brought down 10 mm. below its normal point; the position of the magnet was carefully registered, so that it could be placed in position at a future time.

39. The brass box now was fitted up as in the previous experiment (fig. 23), with a photographic film, E E, at the end, and the magnet put in position. Exhaustion was continued, the coil being turned on occasionally. When the vacuum was high the current was kept going for two hours. On developing the film, only a central spot of action was seen in the middle, but there was no sign of another spot drawn down below it, showing that the rays passing through the aluminium were not deflected by the magnet. This experiment was repeated several times with different exposures and varied forms of apparatus, always with the same result.

40. The explanation of the various results is now clear. The emanations inside the box are Röntgen rays, produced by the impact of electrons starting from the pole A. These electrons, falling on aluminium, a metal of low density and atomic weight, generate Röntgen rays, part of which penetrate the thin metal and radiate from the further surface. Had the metallic disc been made of metal of higher atomic weight, such as lead or platinum, the impact of electrons on it would equally have given rise to Röntgen rays, but these would have been confined almost entirely to the side struck by the electrons (34), and no action would have taken place inside the box.

On the Presence of Europium in Stars.

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(Communicated by Sir David Gill, K.C.B., F.R.S., H.M. Astronomer. Received January 2,—Read January 24, 1907.)

In measures of the radial velocity of α Boötis and β Geminorum, the results for the calcium line at λ 4435·851 (Rowland) are discordant. In both stars, in measures made independently by Mr. Goatcher and the author, the value for this line is too low (positive). The following are the figures :—

α Boötis.

Neg. No.	Measured by author (kilometres per second).			Measured by Goatcher (kilometres per second).		
	Mean shift for plate.	Shift for Ca line.	Diff. Ca line − Plate.	Mean shift for plate.	Shift for Ca line.	Diff. Ca line − Plate.
661	+ 6·81	+ 3·38	−3·43	+ 7·15	+ 3·99	−3·16
672	+15·21	+12·17	−3·04	+14·00	+11·22	−2·78
687	+20·16	+16·22	−3·94	+19·82	+16·83	−2·99
688	+18·94	+17·58	−1·36	+19·53	+15·89	−3·64
689	+20·65	+16·22	−4·43	+20·32	+16·29	−4·03
Mean radial velocity }	− 4·39	− 7·63	−3·24	− 4·58	− 7·90	−3·32

Mean discordance for Ca line, −3·28 kiloms. per second.

For this line a shift of λ 1·0 = 67·60 kiloms. per second. The Ca line, therefore, appears to be 0·049 λ to the violet side of its tabular position.

β Geminorum.

Neg. No.	Measured by author (kilometres per second).			Measured by Goatcher (kilometres per second).		
	Mean shift for plate.	Shift for Ca line.	Diff. Ca line − Plate.	Mean shift for plate.	Shift for Ca line.	Diff. Ca line − Plate.
631	+12·43	+ 7·23	−5·20	+11·08	+ 7·37	−3·71
635	+17·29	+15·55	−1·74	+16·69	+13·72	−2·97
637	+17·59	+16·22	−1·37	+16·95	+14·06	−2·89
643	+20·86	+18·79	−2·07	+21·11	+19·27	−1·84
Mean radial velocity }	+ 4·12	+ 1·55	−2·57	+ 3·56	+ 0·71	−2·85

Mean discordance for Ca line, −2·71 kiloms. per second.

In the spectrum of β Geminorum, therefore, the Ca line appears to be λ 0·040 to the violet side of its tabular position. In a true solar star, a_2 Centauri, this discordance is not apparent.

The stellar line is stronger than the solar line in the two stars first mentioned.

The assumption was made that some line of unknown origin was blended with the Ca line in these stars. On consulting Exner and Haschek's " Haupttabelle," europium was indicated as the disturbing element, a line of intensity 30 being recorded at λ 4435·75.

Assuming the disturbing line to have the same intensity as the Ca line in *a* Boötis, its wave-length from the above measures should be λ 4435·753 which agrees well with the above position of the europium line.

On looking for independent confirmation of the discordant velocity obtained from the Ca line, the following results were found :—

| | | | | Kilometres per second. | | |
| | | | | | | |
Neg. No.	Observatory.	Measured by	Star.	Mean shift for plate.	Shift for Ca line.	Diff. Ca line − plate.
B 293	Yerkes*	Adams	*a* Boötis	−17 ·4	−19 ·5 (1)	−2 ·1
B 304	„	„	„	− 9 ·4	−10 ·7 (2)	−1 ·3
A 373	„	„	„	+11 ·28	+11 ·15	−0 ·13
B 436 {	„	Frost } Adams }	γ Piscium	{ +11 ·20	+10 ·00	−1 ·20
	„			{ +11 ·27	+ 8 ·86 (3)	−2 ·41
B 483 {	„	Frost } Adams }	*ε* Leonis	{ −10 ·20	−14 ·20 (4)	−4 ·00
	„			{ −10 ·00	−12 ·03 (5)	−2 ·03
B 275	„	„	*a* Tauri	+78 ·1	+76 ·1 (6)	−2 ·00
L 2011	Lowell†	Slipher	*a* Boötis	+19 ·30	+17 ·60	−1 ·70
L 2016	„	„	„	+18 ·20	+14 ·00 (7)	−4 ·20
L 2080	„	„	*ε* Pegasi	+21 ·35	+20 ·8	−0 ·55
L 2094	„	„	*a* Arietis	−26 ·08	−28 ·2	−2 ·12

(1), (3), (4), (5), (7).—Extreme value of 21, 16, 14, 16, and 25 lines respectively.

(2).—Extreme value, 18 lines, 10·8 kiloms.

(6).—Extreme value, 17 lines, 75·9 kiloms.

It is to be expected that the discordance of the velocity deduced from this line will vary with different types of stars.

It will be seen that all the measures found agree in placing the stellar line to the violet of the tabular position of the solar line and that the Ca line gives the lowest (positive) radial velocity on many of the plates.

The spectrum of europium does not contain many strong lines in the region of our stellar spectra taken with the 4-prism spectrograph. The

* 'Radial velocities of 20 stars, 1903,' and 'Astroph. Journ.,' vol. 18, p. 268.

† Astroph. Journ.,' vol. 22, p. 331.

following wave-lengths and intensities are given by Demarçay, the discoverer of europium, and by Exner and Haschek :—

Demarçay.[*]		Exner and Haschek.[†]		
			Intensity.	
λ.	Intensity.	λ.	Arc.	Spark.
4130·0	15·5	4129·90	100	100
4173·2	5	4172·98	—	3
4205·4	16	4205·20	100	50
4355·5	7	4355·28	—	3 r
4435·8	16	4435·75	50	30
—	—	4522·76	20	15
4594·5	14	4594·22	—	10
4627·8	13	4627·39	100	8
4662·6	12	4662·08	50	5

The wave-lengths of Exner and Haschek are admitted by Demarçay to be more accurate than the original measures.

On comparing the spectrum of α Boötis with a solar spectrum (daylight), both taken with the same instrument, by placing the negatives film to film and adjusting the lines to coincidence, it was found that the indications of the presence of europium, already noted, were confirmed.

The two strong lines at λ 4129·90 and λ 4205·20 happen to fall on groups of faint lines in the solar spectrum which are unresolved and appear as shadings with the dispersion employed.

α Boötis shows strong lines in the positions given above.

The two faint lines at λ 4172·98 and λ 4355·28 can be neglected as too weak to show themselves in the stellar spectrum.

The line λ 4435·75, as already noted, is stronger in the star than in the sun, making a more equal pair with the Ca, Fe blend at λ 4435·184. The stellar pair also appears as a closer double than the solar pair.

The line at λ 4522·76 does not appear in Demarçay's list, although the fainter spark-lines in Exner and Haschek's Table are included by Demarçay.

Exner and Haschek used a europium nitrate prepared from the oxide supplied by Demarçay himself, who states that his europium is free from samarium, but shows the strongest lines of gadolinium as feeble lines.[‡]

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[*] 'Comptes Rendus,' 1901, vol. 132, p. 1486.

[†] 'Wellenlängen-Tabellen, 1902,' and Watts' 'Index of Spectra, Appendix M.'

[‡] Crookes states that Exner and Haschek's europium was by no means pure, 'Roy. Soc. Proc.,' vol. 74, p. 551, and Crookes' europium from Urbain contained Gd, Y, La and Ca.

Demarçay records a gadolinium line close to this position, and Exner and Haschek record a pair. The discrepancy between the two lists as regards this line is inexplicable. In any case, whether the line is really due to europium or to one of the closely-allied rare-earth metals, it should be noted that the stellar line in α Boötis is stronger than can be accounted for by the iron (enhanced) and titanium lines. It is possible that the Eu (?) line corresponds to the faint solar line, λ 4522·691 Int. 0, marked Fe (?) in Rowland's Tables. Lockyer* identified an enhanced iron line with this solar line, but Reese† subsequently showed that the enhanced iron line is really identical with the next line in Rowland's Tables, λ 4522·802 Int. 3, which has no origin assigned to it. This correction is confirmed by the Cape measures and is accepted by Lockyer.‡

The line at λ 4594·22 falls close to a vanadium line in the solar spectrum, λ 4594·297§ Int. 2 N. In α Boötis this line is markedly stronger than in the sun, perhaps more so than can be accounted for by the vanadium line alone, although it is recognised that the Va lines are intensified in these stars as compared with the sun.‖

Accurate measures of the stellar line, which is sharp, may decide whether it is a Eu, V blend or a pure V line, a point which may be considered doubtful.

The remaining two lines at λ 4627·39 and λ 4662·08 are too faint to give any evidence of much value.

No previous reference has been found to the presence of europium lines in stellar spectra, but after the conclusions here noted were arrived at, it was found that Professor Dyson, Astronomer Royal for Scotland, gives strong evidence for the existence of europium lines in eclipse photographs of the chromosphere.¶

This evidence is the more valuable, as it records the presence of more refrangible strong lines outside the region covered by the four-prism spectrograph, in addition to those already enumerated.

It appeared, also, that in the Report of Mr. L. E. Jewell, on the Pinehurst Eclipse Spectrograms,** the europium origin of certain of the

* 'Roy. Soc. Proc.,' vol. 65, p. 458.

† 'Astroph. Journ.,' vol. 19, p. 331.

‡ 'Roy. Soc. Proc.,' vol. 74, p. 260.

§ Rowland and Harrison, 'Astroph. Journ.,' vol. 7, p. 288, give the λ 4594·216 Int. 10 R for the vanadium line.

‖ Slipher, "Observations of Standard Velocity Stars," 'Astroph. Journ.,' vol. 22, p. 323, and Adams, "Sun-spot lines in the Spectrum of Arcturus," 'Astroph. Journ.,' vol. 24. p. 69.

¶ 'Phil. Trans.,' A, vol. 206, p. 448.

** 'Publications of the United States Naval Observatory,' 2nd series, vol. 4, Appendix I p. D 129, *et seq.*

chromospheric lines corresponding to the strongest lines of that element had been previously queried.

The presence of europium was not, however, positively affirmed.

Demarçay and Exner and Haschek record the following strong lines, more refrangible than those already considered :—

Demarçay.		Exner and Haschek. '		
			Intensity.	
λ.	Intensity.	λ.	Arc.	Spark.*
3724·5	13	3725·08	30	20
3819·5	15	3819·81	50	50
3907·2	14	3907·30	30	30
3930·7	15	3930·65	50	50
3972·0	15	3972·16	50	50

The wave-length tables of Professor Dyson appear to have been derived from photographs showing much finer detail than any others to which reference can be found; he records fainter lines, and shows that many lines elsewhere recorded as single are really blends of two or more lines.

The following figures show that the chromospheric evidence of the presence of europium in the sun is very strong. Jewell's suggested Ni, Fe, Sc, V, and Ba origins do not appear to be supported by the evidence of other lines. The chromospheric lines do not seem fully accounted for without europium.

REMARKS ON THE CHROMOSPHERIC LINES.

(1) Not Ni, compare with Ni line at λ 3858·442. This line is probably due to europium.

(2) Europium line masked by helium, λ 3819·751 Int. 4, Runge and Paschen.

(3) Jewell's Fe, Sc origin suggested for this line is not confirmed by a comparison with the λ 3911·3 chromospheric line corresponding to the stronger Fe, V, Nd, Sc solar group. Dyson's origin seems a much more probable one.

(4) Europium line masked by iron line.

(5) Ni does not account for this line, compare Ni line at λ 3858·442. The line appears to be a pure europium line.

(6) Dyson resolves Jewell's Eu, (?) Fe, Ba line and separates the europium line ; Jewell's line fits Eu better than Fe, Ba.

* In Professor Dyson's paper the headings Arc and Spark are transposed in error.

Europium		Chromosphere					Sun	
Exner and Haschek		Jewell		Dyson		Remarks.	Rowland	
λ.	Int., spark.	λ.	Intensity.	λ.	Intensity.		λ.	Intensity.
3725·08	20	—	—	3724·97	1 He	(1)	3724·970	1 Ni
3819·81	50	3820·5	8 {He, Fe	3819·73	1 Fe	(2)	3819·751	4 He*
				3820·59	7 Ni	—	3820·586	25 Fe-C
		3858·4	000 Ni	3858·35	1 Eu	—	3858·442	7 Ni
3907·30	50	3907·18	0 {Fe, Sc	3907·28	2 Eu	(3)	3907·615	3,dP Fe-Sc
		3908·63	Cr	3908·54	2	—	3908·900	4 Cr
							3910·984	4 Fe-V
		3911·85	000 Fe, Sc	3911·29	0 Nd	—	3911·816	0 Nd
							3911·586	1 Fe
							3911·063	2 Sc
3930·65	50	3930·48	0 Ti, Fe	3930·46	4 Fe	(4)	3930·022	8 Ti
							3930·450	8 Fe
3972·16	50	3972·08	00 {Eu(?), Ni(?)	3972·03	2 Eu	(5)	3972·134	0,N,dP Ni
							3972·818	2 Ni
4129·90	100	4129·82	0 {Eu(?), Fe, Ba	4129·87	4 Eu	(6)	4129·882	1 Fe
				4130·97	2	(7)	4130·196	2 Fe
							4130·804	2 Ba
4205·20	50	4205·09	00 {Eu(?), V(?)	4205·21	6 Eu	(8)	4205·186	1 Ca
							4205·239	1 Fe
4435·75	30	4434·5	00 {Ca, Ca	4434·30	1 Ca	(9)	4435·129	5 Ca
				4435·58	2 Eu(P)		4435·321	2 Fe
							4435·851	4 Ca
4522·76	15	4522·8	00 {Fe, Ti	4522·84	5 Fe	(10)	4522·691	0 Fe(?)†
							4522·902	3 ‡
4594·22	10	—	—	4594·19	1	(11)	4522·974	2 Ti
							4594·297	2 N,V
4627·89	8	4626·9	000 {Cr, Cr	4626·58	0	(12)	4626·096	0 N,Cr
							4626·858	5 Cr

* Bunge and Paschen.   † The iron line coincides with the following line.   ‡ Enhanced Fe (Reese).

(7) Probably barium. The three strongest barium lines given by Exner and Haschek and by Dyson (in chromosphere) are—

Exner and Haschek.		Dyson, in Chromosphere.	
λ.	Intensity.	λ.	Intensity.
3892 ·43	500	3892 ·29	0 —
4130 ·91	800	4130 ·97	2 —
4554 ·21	1000	4554 ·18	7 Ba

(8) Vanadium not likely to enter into this line as stronger lines of V are not represented. Dyson states that V is not at all strong in the chromosphere. Enhanced V line at λ 4205·24, Lockyer.

(9) Europium masked by double Ca line. It is the less refrangible line of the pair which gave rise to this paper. In a Boötis and other stars it is a Ca, Eu blend.

(10) Demarçay gives no europium line here. Place occupied by Fe, Ti.

(11) Possibly a V, Eu blend. Pure europium more probable.

(12) Eu, line may be too weak to show in chromosphere.

As there is such strong evidence of the existence of europium in celestial bodies, it would appear remarkable if the closely allied elements of the rare-earths, particularly samarium and gadolinium, were absent. Professor Dyson records the following rare-earth metals as present, with more or less certainty, in the chromosphere, viz. :—

La, Ce, Pr, Nd, Sa, Eu, Gd, Yb, Y.

Some of these elements, *e.g.*, La, Ce, Nd, Yb, Y are without doubt responsible for lines in the solar spectrum.

The present paper suggests that if the lines of europium are so much more pronounced in the spectra of the more advanced solar stars, such as a Boötis, than in the solar stars proper, the rare-earth metals as a group may possibly account for many of the striking differences to be observed between them.

Lockyer's statements* as to the identity of the sun and Arcturus, both spectroscopically and chemically, require modification.

In these more advanced stars there are so many strongly marked extra-solar lines of unknown origin, which are weak or absent in the solar spectrum, that an accurate list of their wave-lengths would probably be of much assistance to chemists in their search for new elements, of which there must still be many more to discover.

There is great need of more accurate wave-lengths of the lines due to the rare-earth metals. A comparison of these lines with the solar spectrum *on*

* 'Inorganic Evolution,' Macmillan, 1900, pp. 50, 52, 56 and 57.

the same scale as Rowland's maps would not only be valuable in itself, but would be likely to fill in some of the origins in the deplorably long list of unidentified lines in the solar spectrum. The region usually employed in radial velocity determinations might receive first attention.

Note on the Application of Van der Waals' Equation to Solutions.

By the EARL OF BERKELEY.

In a recent communication to the Royal Society[*] by Mr. Hartley and myself, the results are given of some measurements of the osmotic pressures of strong aqueous solutions of cane sugar, dextrose, galactose, and mannite.

It may be of interest to inquire how far these results can be represented by an equation on the plan of that introduced by Van der Waals to express the relation between the pressures, volumes, and temperatures of gases and vapours.

The Van der Waals equation is $(P + a/v^2)(v - b) = RT$, and the two that I have found which fit the present case are

$$(A/v - p + a/v^2)(v - b) = RT, \qquad (1)$$

$$(A/v + p - a/v^2)(v - b) = RT. \qquad (2)$$

The approximation of this form of equation is, perhaps, enhanced when it is taken into consideration that some 50 modifications of Van der Waals' equation were tried. Among these were various possible conceptions which might underlie the meaning of the volume term as applied to solutions, besides modifications of the coefficients a and b, in which these constants were assumed to be some function of either the volume or the pressure. Dieterici's equation of state was also tried with two or three different conceptions of "v."

In the following application of the equations, the units are atmospheres and litres, and R is the gas constant taken as equal to 0.08207. In equation (1) the v is the volume of solvent which contains 1 gramme molecular weight of solute, and in equation (2) it is the volume of solution which

contains the gramme molecular weight. Both of them are derived from the densities of the solutions at 0° C.; and the osmotic pressures, together with the absolute temperature T, refer to that temperature.

In the tables, column I gives the concentration in grammes per litre of solution, II gives the v of equation (1), III the v of equation (2), IV and V the calculated osmotic pressures corresponding to II and III respectively, while column VI gives the observed osmotic pressure.

Cane Sugar.

I. Concentration.	II. v of (1).	III. v of (2).	IV. Calculated osmotic pressure.	V. Calculated osmotic pressure.	VI. Observed osmotic pressure.
850	0·18270	0·39722	(183·0)	(183·0)	(183·0)*
760	0·23656	0·45025	(133·7)	(133·7)	(133·7)
660	0·29883	0·51177	(100·8)	(100·8)	(100·8)
540	0·41431	0·62570	68·4	67·7	67·5
420	0·59471	0·80492	45·0	43·4	44·0
300	0·91883	1·12764	27·7	25·4	26·8
180	1·67368	1·88094	14·6	12·2	14·0

The v's of column II are calculated from Landolt and Bornstein's tables of densities of cane sugar solutions, by finding the change in volume of the solution caused by the addition of 1 gramme of water, and multiplying this by the weight of water which contains 1 gramme molecule of solute. These numbers are given to one significant figure beyond what can here be utilised.

The numbers given in the fourth and fifth columns were calculated, by trial and error, from the equations when applied to the osmotic pressures of the first three concentrations given in the table. The resulting constants were then substituted and the p calculated for the other cases.

The constants for equation (1) are

$$A = 45 \cdot 3689, \qquad a = 3 \cdot 5696, \qquad b = 0 \cdot 05266,$$

while those for equation (2) are

$$A = 6 \cdot 7166, \qquad a = 7 \cdot 2960, \qquad b = 0 \cdot 25139.$$

* This value is derived from vapour-pressure measurements. It will be seen, on p. 505 of the communication referred to above, that all the osmotic pressures, obtained from the vapour pressures, are somewhat higher than those measured directly ; consequently, the osmotic pressure obtained from the vapour pressure of a solution of 850 grammes in the litre was proportionately reduced so as to bring it into line with those measured directly.

Dextrose.

I. Concentration.	II. *v* of (1).	III. *v* of (2).	IV. Calculated osmotic pressure.	V. Calculated osmotic pressure.	VI. Observed osmotic pressure.
549	0·21826	0·32435	(121·2)	(121·2)	(121·2)
449	0·28601	0·39664	(87·9)	(87·9)	(87·9)
319	0·44838	0·55824	(53·2)	(53·2)	(53·2)
200	0·78438	0·89357	28·8	28·4	29·2
100	1·67913	1·78789	12·9	12·4	13·2

The material for calculating the *v*'s of column II in the manner explained for cane sugar was not at hand; as it is known that there is but a small change in volume on dilution, it was considered that the weight of water containing 1 gramme molecule would be close enough for the purpose in view, and it was therefore used. It must be remembered that the dextrose itself was not quite pure,* so that the osmotic pressures are possibly slightly inaccurate.

The calculated osmotic pressures are obtained as in the case of cane sugar and the constants are for equation (1)

$$A = 43\cdot0512, \qquad a = 3\cdot0089, \qquad b = 0\cdot06069;$$

and for equation (2)—

$$A = 3\cdot3845, \qquad a = 2\cdot9706, \qquad b = 0\cdot10762.$$

On comparing the agreement between the calculated and observed osmotic pressures, there seems to be but little difference between the two equations. On the whole, equation (1) appears to be the better fit over the present range; though it is probable that the other one, having the positive sign for *p*, may replace it at high dilutions.

There is apparently another way of testing the ranges of these equations. The system of curves which represent either of them, for different values of T, has features similar to those of the well-known diagram of isothermals for vapour-liquid substances such as carbonic acid. Now, the reasoning originally applied by J. Thomson to Andrews' experiments on gas-pressures admits of extension to the present case. If we draw the system of *p*, *v* curves as mentioned above, then when the temperature is high, *p* will diminish throughout the curve as *v* increases; on passing in succession to curves corresponding to lower temperatures, one will be reached for which the

* *Loc. cit.*, p. 497.

gradient or slope just vanishes at a certain pressure ; and the curves beyond this will have contrary flexure in different parts.

Now, increase of osmotic pressure with increase of dilution must involve intrinsic physical instability, resulting in change of state; and the characteristic equation, together with the derived equations $dp/dv = 0$ and $dp^2/dv^2 = 0$, will determine the critical temperature (and the pressure and volume) below which supersaturation and crystallisation can set in.

The values of T, p, v, for the critical point derived in this way from equations (1) and (2) for cane sugar are impossible ones, being respectively

$$T = 583°\cdot4, \qquad p = -2\cdot01, \qquad v = 0\cdot477,$$

and $\qquad\qquad T = -72°\cdot44 \qquad p = 7\cdot98, \qquad v = 0\cdot612.$

As crystallisation can take place at ordinary temperatures, the p, v curve must show a double bend somewhere near the point at which this occurs; equation (1) shows part of such a bend,* but not equation (2).

We might, therefore, find the point on the curve for T $= 273°$, at which $dp/dv = 0$, where complete instability sets in for that temperature ; but even if the equation held good up to this point, it would merely be the point of maximum possible supersaturation at that temperature, and would not be easily amenable to experiment. Graphs of equation (1) give this upper limit of supersaturation as being at the following values of v :—for cane sugar, $v = 0\cdot092$, for dextrose, $v = 0\cdot12$.

Although equation (2) cannot hold up to the point of saturation, yet, for moderate dilutions, this equation can be inferred from certain theoretical considerations (see *infra*), provided b is the difference between the v's in columns II and III of the tables; this is seen to be the case for dextrose, and not very far different for cane sugar.† The relation ought theoretically to come out better when the value of b is determined from the lower pressures instead of the higher ; the constants A and a, as given above, from the higher observations, seem too big compared with the main term RT.

The point of maximum supersaturation may be estimated in a qualitative way by means of the results obtained with galactose and mannite. The test will probably be still more imperfect, because in the case of galactose that substance was impure,‡ and in the case of mannite the experiments themselves were not very good,§ and also because the observed osmotic

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* These graphs are somewhat similar to that of Van der Waals' equation as applied to carbon dioxide at −20° C.

† It is interesting to note that this value of b for cane sugar in the equation $p(v-b) = RT$ satisfies the lowest observation exactly.

‡ *Loc. cit.*, p. 501.   § *Loc. cit.*, p. 501.

pressures are too close together to define the constants with sufficient accuracy.

Galactose.   Mannite.

I. Concentration.	II. v of (1).	III. Observed osmotic pressure.	I. Concentration.	II. v of (1).	III. Observed osmotic pressure.
500	0·24587	95·8	125	1·3281	16·7
380	0·35660	62·8	110	1·5251	14·6
250	0·60894	35·5	100	1·6897	13·1

The v's under column II are, in both cases, the weight of water containing 1 gramme molecule of the solute.

The constants for equation (1) when applied to galactose are

$$A = 41·90, \qquad a = 2·377, \qquad b = 0·0492;$$

and, from the graph, $dp/dv = 0$ at about $v = 0·095$.

The constants for mannite are

$$A = 38·89, \qquad a = 25·19, \qquad b = 0·494;$$

and $dp/dv = 0$ at about $v = 0·98$.

Thus, finally, notwithstanding the tempting analogy with Van der Waals' equation, shown by the graphs for equation (1) and by the values of b in equation (2), it has appeared that it is only possible to regard these equations, pending further experimental work, as holding good over a limited range of values.

There is one further theoretical consideration which may be touched upon. It is evident that if one could find a membrane which is only permeable to the *solute*, then when the solution is placed in contact with the pure liquid solute through this membrane, an osmotic pressure will be set up. The p, v curves representing these new osmotic pressures and volumes will show phenomena, in connection with the freezing point of the solution, analogous to those discussed above as appertaining to the crystallising point. In other words, the freezing and crystallising points of a solution are two extreme points, with continuous physical transition between them representable by the equations of osmotic pressure.

[*February* 1.—In connection with the preceding paragraph, Professor Larmor has suggested the following generalisation :—

If P is the osmotic pressure, p' the vapour pressure, and T the temperature, then for all aqueous solutions*

$$P = \text{same function of } p' \text{ and T.} \tag{i}$$

Moreover, the freezing point is the temperature for which p', for the solution, is the same as for ice (thus, incidentally, isotonic solutions have the same vapour pressures and the same freezing point). Now, for ice,

$$p' = \text{function of T.} \tag{ii}$$

Equation (i) represents the surface characteristic of water as a solvent; the equation (ii) represents a cylinder parallel to the axis of P. These two surfaces intersect along a curve, which is the freezing curve characteristic of all solutions in water. At each freezing point both P and p' are definite functions of that temperature, the same for all solutions. Thus, to go to a particular case, so far as the equation $P = RT/(v-b)$ holds good—or rather more generally, so far as osmotic pressure depends only on the temperature and on the volume of the water present (with 1 gramme molecule of solute)—then to that extent the freezing point of any aqueous solution depends only on this same volume; *i.e.*, to that extent the freezing point depends only on the concentration of the solution, when estimated on the water present, instead of on the volume of solution. At high dilution it may be taken as simply proportional to this concentration.]

The theoretical considerations that favour the relation (2) for moderate concentrations are, as expressed by Professor Larmor, briefly as follows:— The available (or free) energy of a solution at any given constant temperature can depend only on the ratio of the masses of solute and solvent present; it is, therefore, a function of the ratio of the mass of the solute (a gramme equivalent) to the volume of water present; the latter is $v-b$ where v is the volume of the solution and b may be taken as constant. The general reasoning of Willard Gibbs,† applicable to any very dilute system, shows that this function must be of the form $-C\log(v-b)$. Now the variation of this available energy must be equal to $-pdv$; hence, $p = C/(v-b)$. At extreme dilution b is negligible compared with v, and the usual argument shows that $C = RT$.

* In 'Roy. Soc. Proc.,' Series A, vol. 77, pp. 156—169, Mr. Hartley and I have established the following relation between the osmotic and vapour pressures of a solution—$P = \frac{As}{\sigma}\log_e\frac{p}{p'}$. Owing to some mistake, it was omitted, in that communication, to point out that for a given temperature, as A, s, σ, and p are constants for any one solvent, all solutions which have the same vapour pressures will have the same osmotic pressures.

† J. W Gibbs, 'Scientific Papers,' vol. 1, p. 137.

This reasoning has assumed that the molecular complexes of the solute are so far apart as not sensibly to influence each other directly. We can extend its range to stronger concentrations by introducing a correction for such mutual influence. The argument used by Van der Waals indicates that mutual attraction between the molecules of the solute affects p by the addition of a term $-a/v^2$, while here we have also mutual attraction between the solute molecules and the solvent which is similarly expressible by a term $-A/v$. Thus in the equation above it is $p+a/v^2+A/v$ that should occur instead of p, giving finally $(p+a/v^2+A/v)(v-b) = RT$.

Indeed, without this special explanation we might, perhaps, have asserted at once that the indirect influence of concentration on p must be expressible as a series $-A/v -a/v^2 -e/v^3-.\,.\,.$, virtually as in (2).

It will be of interest to compare the values of b, for which the equation $p(v-b) = RT$ has been found empirically to represent many solutions, by Abegg, Noyes, and others, with the solution-volume of the gramme-equivalent of solute that is concerned ; especially as it has been pointed out[*] that the equation of reaction of Guldberg and Waage can be founded on this latter form of relation as well as on the simple Boyle-Avogadro one.

It will be noticed that the difference between these two types of equation is that the former does not insist on the asymptotic line of the p, v curve passing through the origin, but allows it to pass at a distance b from it measured along the x axis. This freedom is sufficient to account in a general way for the superiority of the first form, when v is still large ; but we have here gone beyond general considerations by giving reasons in favour of a special value of b. The question also remains whether, in the new form, RT actually corresponds to the universal gas-constant; it must do so in gas theory, but the application of the doctrine of available energy to osmotics leaves room for slight discrepancy caused by the attraction of the solvent, such as is indicated in the term A/v *supra*. In the experiments of E. H. Griffiths with cane sugar, at extreme dilution the gas-constant is verified within 0·01 per cent.; this would show that within the range of application of the formula, A cannot be more than about this percentage of RT, which is almost negligible.

I am glad to have the opportunity of thanking Professor Larmor for the kindly advice which he has freely bestowed on this and other work connected with osmotics.

[*] See T. B. Robertson, ' Journ. Phys. Chem.,' vol. 10, pp. 521—528.

The Thermomagnetic Analysis of Meteoric and Artificial Nickel-Iron Alloys.

By S. W. J. SMITH, M.A., A.R.C.S., Royal College of Science, London.

(Abstract.)

The object of the paper is to show how a study of the variation with temperature of the magnetic properties can be applied (1) to the solution of the problem of the composition and structure of meteoric iron, and (2) to throw light upon the changes that take place with change of temperature in the internal structure of nickel-iron alloys.

The paper contains a study in detail of the changes in permeability (for a field intensity of about 0·4 C.G.S. unit) of a typical specimen of " octahedral " meteoric iron when the temperature is altered in various ways between about 0° C. and about 850° C. It contains also a study, for the purposes of comparison, (1) of a sample of " nickel steel " containing nearly the same percentage of iron as the meteorite, (2) of a sample of nearly pure iron. The author desires to express his indebtedness in the experimental part of this work to the assistance he received from Mr. John Satterly.

The specimens used were in the form of rings, and points of importance and interest in connection with the conditions under which the different measurements of permeability and temperature were made are discussed.

An attempt is made to interpret the permeability-temperature curves in terms of the theory of solid solution. The hypothesis of the formation of " mixed crystals " is briefly discussed, and evidence of the connection between permeability and change in the state of crystallisation is given.

The facts already known with respect to meteoric nickel-iron are then summarised, with the object of showing how they can be interpreted by means of the above theory.

Qualitative arguments based upon the results of microscopic and chemical analyses are given to show that the " kamacite " of meteoric iron which shows Widmanstätten figures is the most nickel-rich of one type of nickel-iron crystals, and that the " taenite " is a eutectic mixture of kamacite and of the least nickel-rich of another type of nickel-iron crystals.

The quantitative chemical data are shown to be explicable on the view that kamacite contains between 6 and 7 per cent. of nickel, and that taenite contains between 25 and 30 per cent. of nickel and is a mixture of kamacite and of other crystals containing about 40 per cent. of nickel.

The analogy between the behaviour of supersaturated solutions and of nickel-iron alloys—particularly with reference to recent investigations of the distinction between the " metastable " and " labile " states—is next discussed. It is shown that all the peculiar variations observed in the permeability of the " irreversible " alloys studied can be explained in terms of this analogy and that, if the explanation is correct, confirmation of the modern theoretical view of the conditions of equilibrium between solid solutions and mixed crystals can be obtained from thermomagnetic data.

An essential consequence of the " mixed crystals " hypothesis is that mixed crystals of the nickel-poor type, at the transition temperature, are in equilibrium with a solid solution richer in nickel than the crystals themselves. This conclusion seems to be definitely proved by the thermomagnetic results.

The bearing of thermomagnetic data upon the problem of the composition of meteorites is next considered, and it is shown from these data that the Sacramento meteoric iron is composed mainly of a nickel-iron alloy containing between 6 and 7 per cent. of nickel, and that it contains, in addition, a small quantity of a complex alloy, containing a total percentage of nickel between 25 and 30, of which the nickel-rich constituent contains about 40 per cent. Ni.

The argument in this section of the paper is based upon well-established magnetic principles, and is independent of any theory of solution. It seems to fix, definitely, the existence of a eutectic containing about 27 per cent. Ni in the nickel-iron series. This result, if true, is of fundamental importance in the theory of nickel steels.

The evidence of the changes which occurred in the meteorite, during the course of the thermal treatment, is discussed. Their effect upon the density of the material is shown to be in accord with the thermomagnetic results, and the importance, in any further thermomagnetic investigation of meteorites, of observing the variation of permeability during the first heating is explained.

The origin of the structure of meteoric iron and its relation to the rate of cooling of the material is discussed, in conclusion.

In an appendix, the effect of the first heating to 100° C. upon a new ring of the meteoric iron is given, and shown to confirm the view of the original structure of the meteorite stated in the paper. An interpretation of recent thermomagnetic experiments on nickel steels containing between 30 per cent. and 24 per cent. of nickel (Honda and Shimizu) is also given, and it is submitted that the existence in these steels of the eutectic that occurs in meteoric iron can be demonstrated.

The relation between meteoric and artificial nickel-iron alloys is thus completely revealed and, at the same time, the value of the thermomagnetic method is established.

The Occlusion of the Residual Gas by the Glass Walls of Vacuum Tubes.

By A. A. CAMPBELL SWINTON.

Users of Crookes' tubes for Röntgen ray purposes have for long been aware that, apparently owing to a change in vacuum, the tubes become "harder" with use, and that it becomes necessary in the case of old tubes to heat the glass in order to get the discharge to pass.

In a paper read before the Royal Society in April, 1899,* the present writer pointed out that the vacuum actually increases in cathode ray tubes with use, even if repeated small doses of additional air be let in from time to time.

Villard has also shown that the residual gas in a vacuum tube is driven into the glass, and that portions of the glass of a tube that has been used show bubbles if heated strongly. Again, in a paper on the absorption of gas in a Crookes' tube by Dr. R. S. Willows,† a number of experiments relating to this subject are recorded, including one by Professor J. J. Thomson, in which, after admitting small quantities of air and absorbing the same repeatedly, it was found that the weight of the tube had increased by the weight of the air that had been admitted, although after admission the discharge caused the pressure to fall so much that Röntgen rays were given off by the tube.

The present paper describes certain further investigations on this subject.

The tubes first experimented upon were some of those originally employed by the writer in 1898 and referred to in his above-mentioned paper. Since that date they have been lying undisturbed and open to atmospheric pressure, so that the gas now found to be imprisoned in the glass must have been there for some nine years. No note was taken in 1898 as to the amount of time that the tubes were used, but each was in operation for many hours and under extremely severe conditions, the alternating current employed having a volume of some 20 milli-ampères at about 8000 volts pressure.

The condition of the glass walls of these tubes is now found to be as

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* "On the Luminosity of the Rare Earths when heated *in vacuo* by means of Cathode ays," 'Roy. Soc. Proc.,' vol. 65.
† 'Phil. Mag.,' April, 1901.

follows: When cleaned by rubbing they are quite transparent to casual inspection, though careful examination with the microscope shows that the inner surface of those portions that had been subjected to cathode ray bombardment are materially roughened. When these portions of the glass are strongly heated in a blow-pipe flame, they immediately become clouded, the effect being due to quantities of minute spherical bubbles in the glass, which may clearly be seen with a microscope. The bubbles vary to some extent in size, but on the average are about 0·01 mm. in diameter. They are usually packed closely together in a single layer and are always very near the side of the glass that formed the inner surface of the tube. On measuring the thickness of the glass with a micrometer gauge, dissolving the inner surface with hydrofluoric acid until the bubbles had just disappeared, and then again measuring the thickness, it was found that, after making allowance for the size of the bubbles, the centres of these bubbles were about 0·122 mm. from the inner surface of the glass. A similar estimate was obtained by grinding the inner surface of the glass until the bubbles just disappeared and making micrometer measurements as before. It would therefore appear that the particles of gas must have been shot into the glass to about the depth stated.

In a typical piece of glass the number of bubbles per square centimetre of glass was found to be about 625,000, so that, allowing for the expansion of the gas on heating the glass up to redness, there was occluded about 0·000113 c.c. of gas at atmospheric pressure per square centimetre of glass, and as the amount of glass surface that was bombarded in each tube was about 400 sq. cm., the total amount of gas at atmospheric pressure occluded in each tube is nearly 0·05 c.c., apart from any further amount that may have escaped from the glass in the heating of the latter.

An interesting question arises as to whether the gas is merely mechanically mixed with the glass or whether there has been any chemical combination between the two. In the latter case, it seemed unlikely that mere powdering of the glass would cause the gas to come out, while in the former case it seemed probable that powdering the glass would have this effect.

In order to test this, a number of pieces of the glass were placed in a chamber consisting of two slightly dished tinned plates some 15 cm. in diameter, which were soldered together all round the edges, with a metal tube inserted, so as to be air-tight. The chamber was connected with a mercury pump and a spectrum tube, and was then pumped until no electric discharge could be got to pass through the spectrum tube. An anvil was then placed under the chamber and the latter was struck several blows with a hammer so as to powder the glass, when there was an immediate fall

of vacuum, and on examination with a spectroscope the gas that had been evolved was found to be mainly hydrogen. The chamber was then pumped out again, and on further blows being struck so as to powder more glass, similar results were obtained; in fact, the process was repeated many times, the result being in each case to bring out more hydrogen.

It would appear, therefore, that the gas occluded in soda-glass vacuum tubes exhausted in the ordinary manner from air is almost entirely hydrogen, no doubt due to electrolysis of water vapour condensed on the walls of the tube prior to exhaustion, the oxygen of which is absorbed by oxidation of the aluminium electrodes.

In order, further, to determine whether the occlusion of gas in a vacuum tube is in any way due to chemical combination of the gas with the glass, or whether it is purely a case of the gas being driven into the glass and mechanically held there, a suggestion made to the writer by the Hon. R. J. Strutt was followed, and experiments were tried with helium.

A spherical tube of soda glass about 7 cm. in diameter, with two electrodes consisting of aluminium plates, was employed. The tube was first exhausted in the ordinary way from air until the vacuum was so high that the discharge would not pass, and then, by an arrangement of stop-cocks, a small quantity of helium was admitted. The tube was then sparked and the vacuum was found to increase, showing that the helium was being absorbed. Further small quantities of helium were admitted at intervals, the process being continued intermittently for 20 days, the total number of hours of sparking being about 90, or 4½ hours per day, and the number of admissions of helium about 700, until about 1 c.c. of helium at atmospheric pressure had been absorbed.

During the process of sparking the tube gradually blackened, the deposit being afterwards ascertained to be aluminium from the electrodes. There thus seemed some doubt as to whether the helium was being absorbed entirely by the glass or perhaps partly by the very thin coating of aluminium, which, by the time the cubic centimetre of helium had been absorbed, had become a perceptible mirror.

On breaking up the tube, however, it was found that whether the glass was heated without further treatment, or whether the mirror of aluminium was first dissolved off its surface with dilute nitric acid, a plentiful supply of bubbles was produced in the glass, showing that at any rate some portion of the helium had found its way into the latter. In appearance the bubbles were very similar to those that had been found in the tubes that had occluded hydrogen, only, as a rule, the bubbles were more numerous and considerably smaller in diameter. Furthermore, as a rule, they tended to be

gathered together in groups and were not evenly distributed over the glass as in the case of hydrogen.   Under these circumstances, it was very difficult to estimate the quantity of gas occluded in the glass.   It was certainly much less than in the case of hydrogen, and only a fraction of the 1 c.c. occluded altogether.   The remainder would seem not to have been driven far enough into the glass to form bubbles, but to have escaped from the surface on the glass being heated.

Similar experiments were made with the glass containing helium to those tried with the glass containing hydrogen, in the way of extracting the gas by powdering the glass in a vacuum chamber.   It was found impossible to get rid altogether of the hydrogen spectrum and other faint lines, due, no doubt, to impurities, but, on the glass being powdered, the helium spectrum was found to be clearly superposed.   This was equally the case when glass that was still coated with the aluminium deposit was used as with glass from which this deposit had been dissolved off.   Consequently, the occlusion appears to take place entirely in the glass.

Seeing that helium does not combine with anything at ordinary temperatures, and seeing further that it could be extracted from the glass by the mere mechanical powdering of the latter, it would appear that the occlusion is due to the mechanical driving of the gas into the glass and not to any chemical combination.

The writer is indebted to Mr. J. C. M. Stanton and Mr. R. C. Pierce for their assistance in carrying out the investigations.

A Recording Calorimeter for Explosions.

By BERTRAM HOPKINSON, Professor of Mechanism and Applied Mechanics in
the University of Cambridge.

The determination of the rate of loss of heat to the walls of a vessel after
an explosion within it is a matter of considerable scientific interest and of
practical importance. Hitherto such determinations, if we except the recent
work of Dugald Clerk on the loss of heat in the gas engine cylinder, have
been based upon a study of the fall of pressure during the cooling of the gases
after the explosion. From the pressure the mean temperature can be
deduced, and thence, if the specific heat is known, can be found the rate of
heat loss at any moment. Such a calculation is, however, obviously unsatis-
factory, because the only available values of the specific heat of gases at
temperatures above 1500° are based upon explosion experiments, and involve
doubtful assumptions as to the amount of loss before combustion is complete.
Some means of determining the loss of heat at any instant without any
knowledge of specific heat is therefore essential, both for finding the law
of cooling of hot gases confined in a closed vessel and for placing on a satis-
factory basis the specific heat values obtained from explosion experiments.
I have devised a simple means of doing this which appears to be capable of
considerable accuracy. It consists essentially in lining the explosion vessel
as completely as possible with a continuous piece of copper strip and
recording the rise of resistance of the copper strip during the progress of the
explosion and the subsequent cooling. Knowing the temperature of the
copper and its capacity for heat, the heat that has flowed into it from the gas
may be calculated from the resistance, certain corrections being applied for
the heat which the copper has lost to the insulating backing.

Up to the present I have only used the apparatus for the investigation of
the loss of heat after an explosion of coal gas and air, but it might, I think,
be applicable, with certain modifications, to finding the heat loss during and
after the combustion of solid explosives.

The explosion vessel is shown in section in fig. 1. It consists of a cast-iron
cylinder 1 foot in diameter and 1 foot in length on to which are bolted two
end plates. The cylinder was first completely lined with wood ¼ inch thick,
and the end plates covered with pieces of cork. Thirty-nine turns of copper
strip of the quality used for electric lighting purposes, and of a high degree

of purity, were then wound on the inside of the curved portion, a clearance of about 1/20 of an inch being left between successive turns. The strip was ¼ inch wide by 1/25 inch thick. The ends of this piece of strip were brought to terminals outside the vessel. The end plates were similarly covered
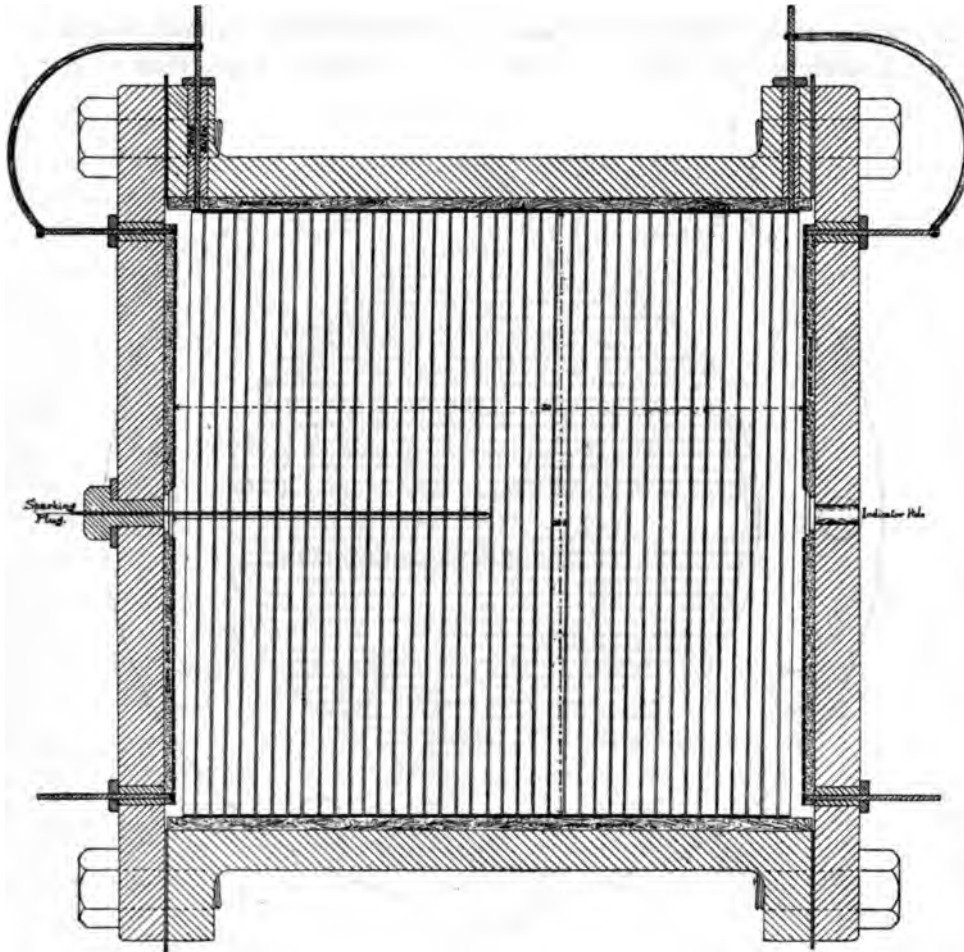
FIG. 1.

with parallel pieces of copper strip of the same dimensions, as shown in fig. 2, the ends being brazed to connecting pieces. The strips on the ends were electrically connected outside the vessel to the strip in the cylindrical part. The whole when put together formed an explosion vessel having a capacity of about 0·684 cubic feet which (except for the uncovered portions on the ends where the cocks, etc., came through) was completely lined with an electrically continuous length of copper having an approximately uniform section of

1/100 of a square inch. For recording the pressure I used an optical indicator, consisting of an iron piston which was forced by the pressure against a piece of straight spring held at the ends. The displacement of the spring tilted a mirror about a fulcrum, and the mirror cast an image of a fine hole illuminated by an arc lamp on to a photographic film carried on a revolving drum. This indicator was repeatedly calibrated by dead weights, and I think its readings are to be trusted to within 1 per cent. of the
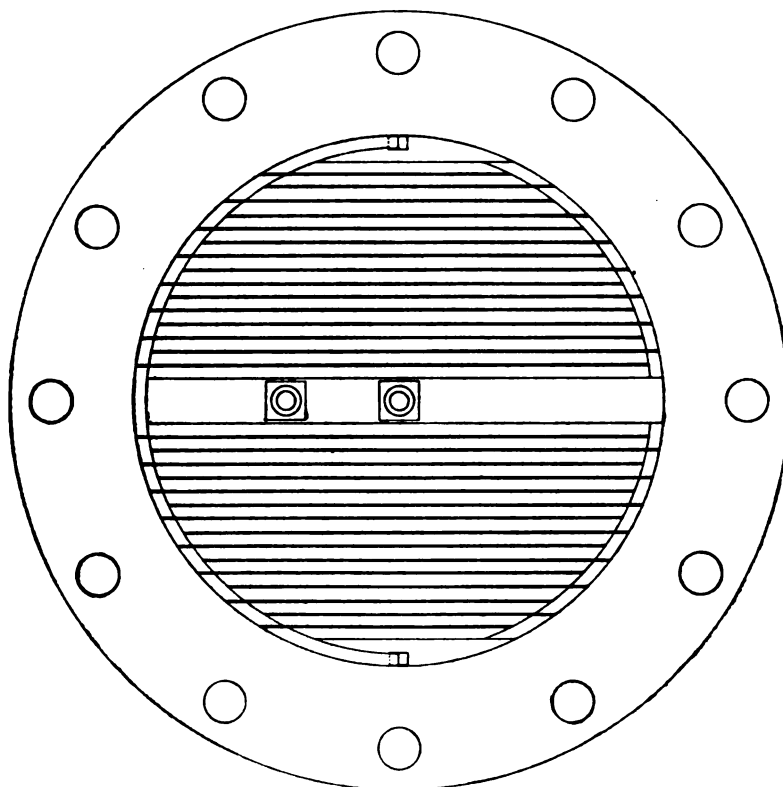
FIG. 2.

maximum reached. The mixture was fired by an electric spark at the centre of the vessel, and it was at atmospheric pressure and temperature before firing.

For recording the temperature of the strip, it was connected as shown in fig. 3. G is a D'Arsonval galvanometer having a stiff suspension and a periodic time of about 1/15 of a second. Its resistance is 3·2 ohms. It is placed in series with the copper strip and with a resistance R of about ¼ of an ohm. A constant current of about 8 ampères is maintained in the strip

by means of the battery B_1 (50 storage cells) and the bank of lamps L. A constant current of about $4\frac{1}{2}$ ampères is maintained in the resistance R by means of the battery B_2 (six storage cells) and an external resistance R_1, the current being in such a direction that the E.M.F. at the terminals of R opposes that at the terminals of the strip. The resistance of the strip S being 0·14 ohm at the temperature of the room, the result of this arrangement is that there is an approximate balance of electromotive force in the

L

B_1

8 Amps.

S

0·25 Ohms

R

R_1

$4\frac{1}{2}$ Amps.

G

B_2
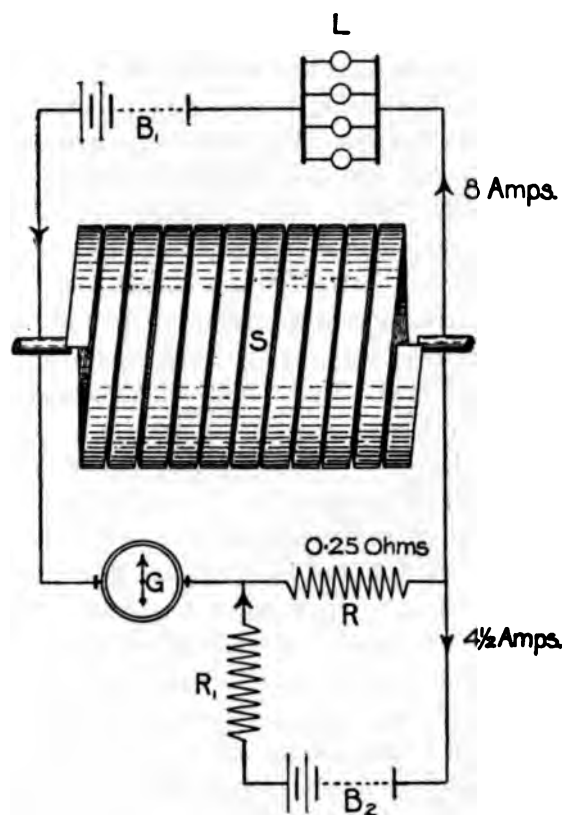
FIG. 3.

galvanometer circuit before the explosion, and the galvanometer then shows little or no deflection. When the explosion takes place the copper strip S is heated and its resistance rises, and since the current in it remains constant during the short time occupied by the cooling of the gas to ordinary temperatures, the potential at the terminals of the strip rises by an amount proportional to the increase of resistance or to the increase of temperature. Since the potential at the terminals of the resistance R remains constant, except for the small disturbance due to the passage of the galvanometer

current, the galvanometer deflection from the reading just before the explosion will be proportional to the rise of potential between the terminals of the strip or to the rise of temperature. The mirror of the galvanometer reflected on to the moving film an image of the same small hole as was used for recording the change of pressure, and a simultaneous record was thus obtained of the change of temperature of the strip and of the pressure in the vessel.

One such record is shown in fig. 4. Curve A is the pressure reckoned downwards from the atmosphere line A_0. Curve B is the galvanometer deflection reckoned upwards from the zero line B_0.* The galvanometer is thrown into slight oscillation, owing to the very rapid change of temperature which occurs when the hot gas first comes into contact with the strip. The white dots on the lines are due to the fact that an alternating current arc was used for illuminating the hole; they are very useful in measuring the diagrams, because they enable corresponding points on the two curves to be identified correct to about 1/500 of a second. On the pressure curve A, 1 mm. deflection corresponds to a pressure of 1·80 lbs. per square inch.† The barometer in this case stood at 753 mm., equivalent to 14·6 lbs. per square inch. The temperature just before explosion was 15° C., or 288° absolute. Allowing for the contraction of volume of 3 per cent., which occurs in the combustion of a mixture of one part of Cambridge coal gas and seven parts of air, it follows that 1 mm. on the pressure diagram corresponds to a rise of temperature of 36°·6 C. On the curve B_1, showing the galvanometer deflection, 1 mm. is equivalent to a rise of resistance in the strip of 0·00047 ohm, or to a mean temperature rise of 0°·83 C., assuming a temperature coefficient of 0·00428. The total weight of strip is 2870 grammes, and the specific heat is taken as 0·093; the quantity of heat corresponding to 1 mm. on the galvanometer curve is, therefore, 222 calories. The values assumed for the heat capacity and temperature coefficient are probably very nearly correct, since the strip is nearly pure copper; but it is difficult to determine them directly with sufficient accuracy. In order to confirm their correctness as far as is necessary for the present experiment, a portion of the strip was wound on a wooden frame and was electrically heated by passing a current of about 350 ampères through it

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* The doubling of the zero line is due to the fact that the mixture failed to ignite at the first attempt. The current was left on for a minute or so while this was being investigated, and slightly heated the strip. At the second (successful) attempt the position of the zero line had therefore shifted upwards to an extent corresponding to the rise of temperature.

† All measurements refer to the original film. The reproduction is approximately three-quarters of the original size.
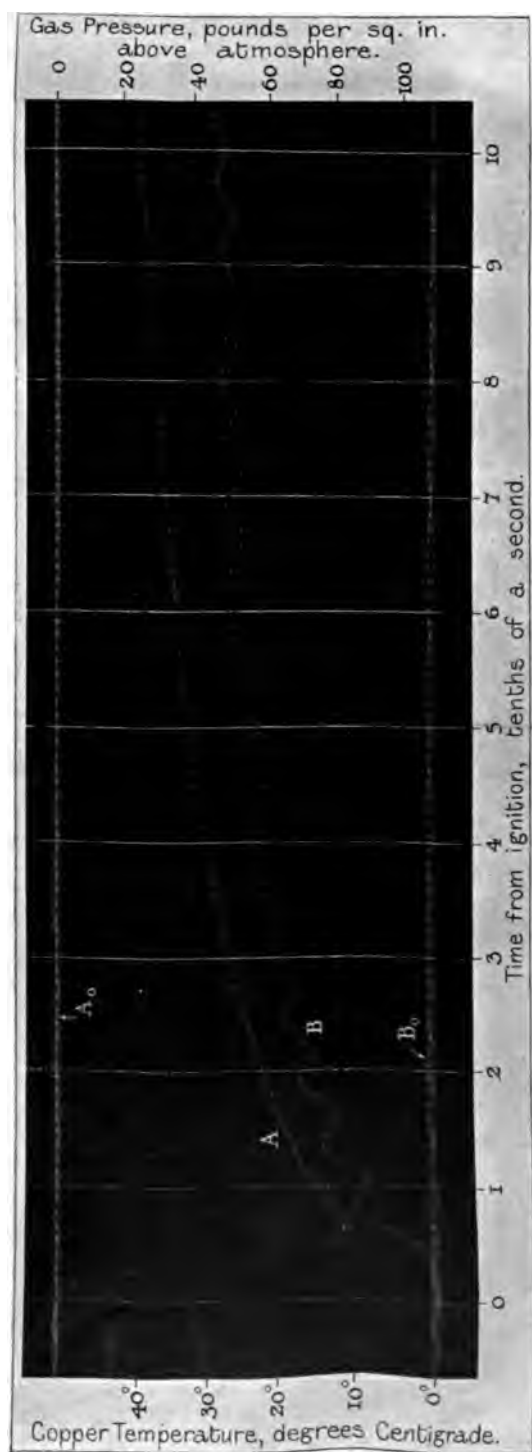
Fig. 4.

for 1·4 seconds. The amount of energy put into the strip in this process was measured by a ballistic wattmeter, the suspended coil of which was placed (with a high resistance in series) as a shunt across the terminals of the strip, while the fixed coils carried the current. The resistance was measured just before and just after the passage of the current. In this manner a direct relation was established between the energy put into the copper and the rise of resistance produced thereby. It was found to be the same, within 1 per cent., as that deduced from the assumed temperature coefficient and specific heat.

Of the heat which passes into the copper, some part is lost to the wooden backing behind it, and it is the balance only which is directly measured in the diagram. The percentage of heat so leaking out is a correction which increases from less than 1 per cent. 0·1 second after firing up to about 20 per cent. 1 second after firing. In order to determine the amount of this correction, recourse was had to the method of electrical heating described above. A current of about 350 ampères was passed through the strip in the cylindrical part of the vessel for 1·4 seconds, and the resistance was determined immediately after the current ceased. The amount of energy put in under these circumstances was found to be 17·5 per cent. greater than the heat accounted for by the rise of temperature in the copper strip. The loss of heat to the backing was therefore 0·175 óf that which had gone into the copper. The loss of heat depends on the manner in which the temperature of the copper rises, which is not quite the same in the explosion vessel as in the electrical heating. In the latter case the rate at which work is done on the copper is nearly constant, and the temperature rise is nearly proportionate to the time, whereas after the explosion the temperature rises at first very rapidly and then remains more nearly constant. By the methods of the Fourier analysis of the conduction of heat, however, if the loss of heat for any one surface variation of temperature is known it can be calculated for any other. The surface temperature of the wood is the temperature of the copper. We determine experimentally the flow of heat into the wood when its surface temperature is made (by electrical heating) to vary as a linear function of the time. From the result is calculated the heat-flow when the temperature varies in the manner given by Curve B in the diagram. Details of these and other calculations are given at the end of the paper.

In addition to the heat which passes into the copper and, *viâ* the copper, into the backing behind it, heat also goes into those parts of the walls which are not covered. The total exposed area covered by the copper strip is 3200 sq. cm. The total surface of the vessel is 4000 sq. cm. There are therefore 800 sq. cm., or about 1/5 part of the total, uncovered. Of the

uncovered area, however, approximately 580 sq. cm. are the narrow strip left for insulation between the adjacent turns or pieces of copper strip. These turns are separated by 1·15 mm. on the average, and since the thickness of the strip is 1 mm., any gas that reaches the backing which is exposed between the turns must part with the greater part of its heat to the edges of the strip. This part of the uncovered area may be regarded as protected by the copper, though not actually covered by it.

The balance of 220 sq. cm. consists mainly of two large patches on the end-plates, and of an annular space round the copper on each end-plate. It will receive heat at approximately the same rate, on the average, as does the copper. The whole heat which the gas has lost, therefore, exceeds that which has gone into the copper in the ratio 4000/3780, or by 6 per cent. This correction is the most uncertain point in the whole experiment. It is under-estimated, because some heat, no doubt, finds its way between the turns. But the error on this account cannot be very large.

As a preliminary test of the accuracy of the copper strip calorimeter, I have calculated the heat accounted for by it at points so far down the cooling curve that the specific heat of the gas may be considered as known. We may take, for example, a point about 1 second after ignition, when the gas temperature is 545° C. At this point the ordinate of Curve B (after smoothing the oscillations) is 35·3 mm., equivalent to 7850 calories. The correction to be added for loss of heat to the backing (see Appendix 2) is here 20 per cent.; the total heat which has passed into and through the copper is therefore 9420 calories. Multiplying this by the factor 1·06, we get 10,000 calories as the heat which has gone into the walls.

Before firing, the mixture was of the following composition, approximately :—

Cambridge coal gas	0·082 cub. ft. =	12·7	per cent.
Air (including some water vapour)	0·565 „ =	87·3	„
Total	0·647 „ =	100·0	„

the volumes being reckoned at 0° C. and 760 mm.

The calorific value of the gas, determined in a Boys calorimeter, was found to be 670 British thermal units, or 170,000 calories per cubic foot. The heat produced in the explosion is therefore 14,000 calories, if the products are all cooled to about 15° C. If we suppose the cooling to be stopped at 545° C., the heat evolved will be less by the latent heat of the steam produced (about 30 grammes per cubic foot of coal gas) and by the amount evolved by the gaseous constituents in cooling from 545° to 15° C. The

latent heat item is $600 \times 30 \times 0.082 = 1480$ calories. For the other item we must have recourse to the results of Holborn and Austin, who have determined the specific heat of steam, CO_2, and air by direct heating at constant pressure up to 800° C. These results are shown in the second column of the following table, which also gives the composition of the products present in the explosion vessel and the heat evolved by each in cooling through the range named. The specific heats are expressed in calories per cubic foot at constant volume, and are the mean values between 15° and 545° C. The amount of steam is not accurately known, since no measurement was made of the degree of saturation of the gas and air before combustion; moreover, the steam does not all condense at the lowest temperature of 15°, and some of it is, therefore, not cooled through the full range as gas. But the error on either account is very small.

	Amount.	Specific heat.	Heat evolved in cooling 530°.
CO₂...............	0·046	10·7	260
Steam	0·118	8·4	527
N and O	0·460	6·3	1540
Total	0·624		2327

Adding the heat of condensation (1480 calories) we get 3807 calories evolved in cooling the products of the combustion from 545° to 15° C. The heat evolved by the products of the explosion in cooling down to 545° C. is then 14,000—3807, or say 10,200 calories. This agrees very closely with the heat found by the copper strip calorimeter, viz., 10,000 calories.

As a further check, we may make a similar comparison at the end of half a second from the time of firing. At this point the gas temperature obtained from the pressure diagram is 840° C., which is just beyond the limit of Holborn and Austin's specific heat determinations. At this point we have:—

Heat in copper strip, 30¼ mm. ....   6720 calories
Heat lost to backing, 12 per cent. of the above   810   „
Heat to uncovered part, 0·06 × 7530...............   450   „

Total heat lost to walls   7980   „

The heat evolved in cooling the products from 840° to 15° C. and in condensing the steam is 5180 calories. The heat evolved in cooling the burnt products to 840° should, therefore, be 14,000—5180 = 8820 calories.

According to this estimate, therefore, the copper strip calorimeter is about 800 calories, or 10 per cent. wrong.

There is, however, a considerable possible error in the estimate derived from the calorific value of the gas at this point. In the first place that calorific value may itself be in error by as much as 2 per cent., or 280 calories. Again, Holborn and Austin consider that their measurements of specific heat may be in error by as much as 3 per cent., equivalent to a possible error of 120 calories in this experiment. Finally, it is possible that some of the gas is still unburnt. There are several small passages connected to the vessel, and there is a small annular clearance space between the end-plate and the end of the wooden lining of the cylindrical part. These spaces amount in the aggregate to only 1 per cent. of the whole volume of the vessel, but they are so situated that in the progress of the flame unburnt gas is compressed into them. Thus at maximum pressure these places will be filled with unburnt mixture at a pressure of about 7 atmospheres. On account of the large cooling surface in these places it is probable that the flame does not penetrate into them at once; the gas trapped in them burns slowly, coming out of its retirement into the main body of the vessel as the pressure falls, and then burning. At time 0·5 second the pressure is 3 atmospheres, and there may still be as much as 2 or 3 per cent. of the mixture remaining unburnt in the spaces referred to. Since 3 per cent. of the mixture represents 420 calories, this goes far to account for the discrepancy between the observed and calculated values of the heat loss.

These experiments establish, I think, the substantial accuracy of this form of calorimeter. The most uncertain feature is the allowance to be made for the uncovered area. This has been taken as equal to 6 per cent. of the covered area, which is an inferior limit. The close agreement of the calculated and observed values of heat loss, 1 second after firing, shows that this allowance is not far wrong. The other correction, that of the loss of heat to the backing, though far larger in amount, is capable of pretty accurate determination. It rests really upon a comparison of the rise of resistance produced by the application of the same amount of work to the copper strip when exposed to the air and when in contact with the backing. It is independent of the absolute meaning of the ballistic wattmeter readings and of any knowledge of the specific heat or temperature coefficient of the copper.

The Law of Heat Loss.

The full line curve, fig. 5, shows the heat loss per square centimetre of surface in terms of the time. This is curve B of fig. 4, with the oscillations

smoothed out and corrected for the loss of heat to the backing. It may be noted that only the absolute values on this curve are affected by the uncertainty as to the effective area of the copper. The comparative heat losses at different times are no doubt accurately shown. This determination of heat loss is, of course, quite unaffected by the uncertainty as to when combustion is complete.

The loss of heat begins about 1/20 second after ignition, when the flame
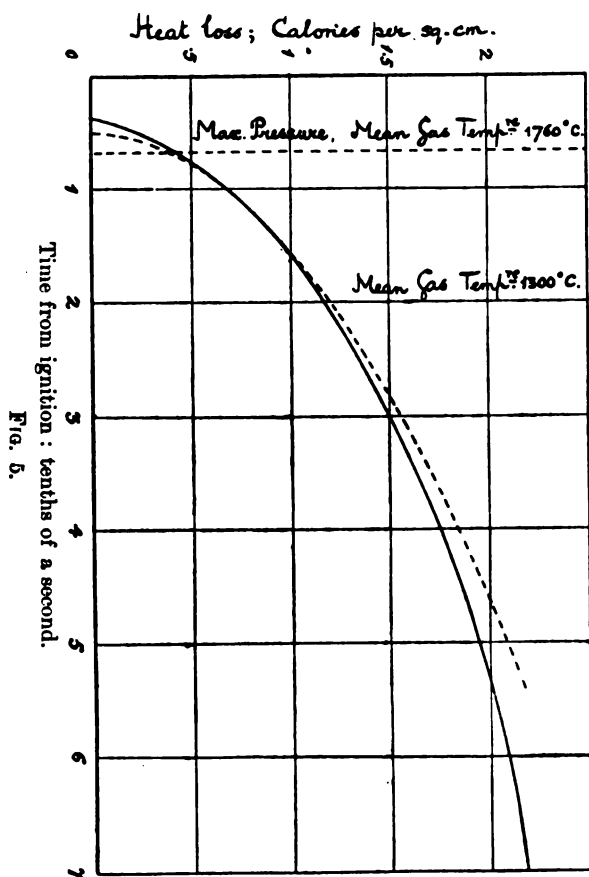
first comes into contact with the copper. At first the loss goes on at a very great rate, and by the time maximum pressure is reached (when the flame is in contact with the whole surface of the strip and losing heat to every part of it), about 1700 calories, or 12 per cent. of the gross heating value of the gas, has passed in to the walls. The rate of loss of heat at this point is about 10 calories per second per square centimetre, and the mean gas temperature is 1760° C. At 0·2 second from ignition the rate of heat loss

is about $3\frac{1}{2}$ calories per second, and the mean gas temperature is 1300° C. The mean temperature is reduced in the ratio 0·74 between these two points, the product of mean temperature and pressure is reduced in the ratio 0·55, but the rate of loss of heat at 0·2 second is only 1/3 of what it is at maximum pressure.

A study of these figures brings into prominence one aspect of cooling after an explosion, which has, I think, hardly received the attention it deserves. The immediate effect of the explosion is to raise the temperature of the mass of gas to a mean value of about 1800° C., and the boundary of this hot body is suddenly cooled by contact with the walls to about 15° C., which surface temperature remains practically constant during the time of cooling. The heat passing in to the walls immediately after the flame touches them is drawn almost wholly from the surface layer of gas in contact with them, and as it has to be transferred so short a distance its flow is at first extremely rapid. This surface layer, however, soon parts with its heat, and further supplies have to be drawn from the inner portions of gas, the cool surface layer now acting as heat insulation. Thus the rate of flow rapidly diminishes.

The cooling of the mass of flame may, in fact, be expected to follow substantially the same law as that of a solid body similarly treated. The Fourier analysis shows that if the surface of a body of large extent uniformly heated to temperature θ be suddenly cooled to temperature zero, and the surface temperature then maintained constant, the heat-loss per unit of surface up to any time t will be at first proportional to the square root of the time, being equal to $2\theta \sqrt{\dfrac{kct}{\pi}}$, where k is the thermal conductivity and c the thermal capacity per unit volume of the solid. Strictly true of a body of infinite extent having a plane boundary, this law holds approximately for finite bodies so long as the central portions have not been much cooled. It is interesting to enquire how far the cooling of the flame follows the same law.

On fig. 5 I have shown in dotted line a curve whose ordinate is proportional to the square root of the time, reckoned from a point 0·05 second after ignition. This point was chosen because loss of heat does not begin at all points of the strip at the same time; the flame first touches the strip about 0·035 second after ignition, and it is not in contact with every part until 0·065 second after ignition. It will be seen that except for the first fiftieth of a second the two curves agree well up to about 0·3 second, when the heat loss becomes considerably less than if it followed the square root law. This would equally happen with a solid body of finite dimensions when

the cooling had penetrated to the interior; the square root law only holds accurately for a body of infinite dimensions.

The Fourier analysis is strictly applicable only to a solid body in which heat transfer takes place only by conduction, and in which the thermal capacity and conductivity are independent of temperature. In the gas, the transmission of heat takes place mainly by convection. The effects of convection may probably be mathematically represented in very much the same way as those of conduction; convection consists in the bodily transfer of gas from a place of high temperature to a place of low temperature, and the corresponding rate of transmission of heat will, for a given amount of agitation, be roughly proportional to the temperature gradient. There will be an effective conductivity k, depending mainly on the state of motion of the gas. But though in a general way the loss of heat may be expected to go on in the gas according to much the same laws as in the solid body, the differences between the two cases are so great that there is not much *a priori* ground for expecting exact quantitative agreement. The closeness with which the loss of heat after the explosion follows the square root law may be to some extent accidental, and hardly in itself justifies making quantitative applications of the same kind in other cases. It seems to me, however, to justify drawing a few general inferences. The most important is that the rate of loss of heat from a hot gas is not only a function of the mean pressure and temperature, it really has very little to do with these quantities. It is dependent essentially on the temperature gradient in the surface layer just within the walls, and this, in any practical case, is mainly determined by the history of the surface layer. No valid inference as to the rate of loss of heat after an explosion can be drawn from experiments on heat conduction or convection in a gas under steady conditions of temperature. Nor can it be assumed that two masses of gas, in similar vessels and at the same pressure and mean temperature, will lose heat at the same rate, though that assumption is often made. Another point is that the rate of heat loss may be expected to increase considerably with the density of the hot gas, the temperature and state of agitation being the same. According to the solid body theory, the rate of loss of heat is proportional to $\sqrt{kc}$. Now in a gas c, the thermal capacity per unit volume is proportional to the density. Moreover k, the effective conductivity, may also be expected to increase more or less in proportion to the density. For k represents the rate of heat transfer by the motion of the hot gas, and the quantity of heat carried by a given volume of gas at a given temperature is proportional to the density. It would not be surprising if the loss of heat after an explosion were found to be proportional to the density of the gas

in spite of the fact that experiments under steady conditions of temperature show that the rate of removal of heat from a hot body by gas surrounding it does not increase in proportion to the pressure of the gas. I think it possible that a good many hitherto obscure phenomena connected with explosions may be explained by considerations such as these.*

Specific Heat Determinations.

By deducting from the total calorific value of the gas the heat lost up to any moment as determined by calorimeter, the internal energy (thermal and chemical) in the gas at that moment can be obtained. Since the mean

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* *February* 11, 1907.—Since writing the above I have had the advantage of reading two papers by Lord Rayleigh ('Phil. Mag.,' March, 1899). In one of them he investigates mathematically the law of cooling of a mass of air by conduction, when the surface temperature is suddenly changed, the air being enclosed in a spherical enclosure of constant volume. The Fourier analysis is applied with the modifications necessitated by the fact that when any portion of the air is cooled below the temperature of the remainder it contracts and thereby causes all the other parts to expand, so lowering their temperature in a manner independent of conduction. It is shown that if the radius of the sphere be 16½ cm. the excess of the mean temperature of the air over that of the surroundings will fall to half its initial value in 26 seconds. In the second paper, experiments are described in which this result is verified, by observing the rate of fall of pressure in a mass of air, contained in a spherical enclosure, after it has been suddenly heated by adiabatic compression.

The experiment is closely analogous to observing the fall of pressure after an explosion, with the difference, however, that the range of temperature is only a fraction of a degree Centigrade as compared with 1000° or 2000°. The mathematical analysis only applies when the range of temperature is small. It is, however, interesting to compare the rate of fall of temperature in the two cases. My explosion vessel happens to be of about the same dimensions as the sphere in Lord Rayleigh's experiments, and it will be seen from the pressure-curve (fig. 4) that the pressure falls to about half of its maximum value in 0·38 second, that is, in about 1/70 of the time taken for a similar amount of cooling in Lord Rayleigh's experiments. This result must be ascribed mainly to the effects of convection after the explosion; for neither the thermal conductivity nor the thermal capacity (which is the other constant determining the rate of fall) is very greatly different in the two cases. It is known that the gases are set into violent vibratory motion by the explosion, and it seems possible that the greatly enhanced "effective conductivity" is due to this fact. Possibly, radiation may also play some part in accelerating the cooling.

The curve of heat loss, calculated by Lord Rayleigh for the spherical mass of air, agrees fairly well with a curve whose ordinates are proportional to the square root of the time, until the temperature has fallen to about 0·6 of its initial value. The fall of temperature in half that time is very nearly 0·75 of the fall occurring in the whole time. If it went as the square root of the time the ratio would be 2−½ or 0·71. After the explosion the temperature falls to 3/5 of its maximum value in about 0·3 second from the time of ignition, and, until then, the curve of heat loss is closely similar to Lord Rayleigh's curve, the deviations from the square root law being in the same direction and of about the same amount.

temperature of the gas is known a curve of specific heats at all temperatures up to 1800° C. could thus be obtained. To use Dugald Clerk's phrase, however, these would be "apparent" specific heats, involving the assumption that all the gas is burnt. Now, though that assumption may very likely be true for a vessel with a smooth surface and without pockets, it is certainly not true in the vessel with which I experimented, and in which, as indicated above, the gas trapped in the pockets is a serious proportion of the whole. I will, therefore, defer all discussion of the information which this calorimeter may be expected to give as to the variation of specific heats, until I have fully investigated the question of delayed combustion.

I desire to acknowledge the very able assistance that I have received in this investigation from Mr. L. du B. Hugo, who was until lately a student and assistant demonstrator in the Engineering Laboratory, Cambridge. He carried out most of the experimental work under my direction, and made several suggestions which materially facilitated it. I have also to thank Professor Callendar for the kind interest which he has shown in the work.

APPENDIX.

1. *Temperature Distribution in the Copper Strip.*

Different parts of the length of the strip receive heat at different rates, but the total heat given to any element of length is equal to the rise of temperature of that element multiplied by its thermal capacity. Since the strip is of uniform section from end to end, the thermal capacity of an element is proportional to its length. For the same reason the increase of resistance of an element is proportional to the rise of temperature multiplied by the length. The rise of resistance of the whole length, therefore, measures the heat given to the whole length, provided that the temperature may be assumed uniform over the section.

This assumption can be readily justified. The thermal conductivity of copper may be taken as 0·9. At maximum pressure heat is flowing into the copper, according to the curve, fig. 5, at the rate of about 10 calories per square centimetre per second. The corresponding temperature gradient just within the surface of the copper is 11° per centimetre. If this temperature gradient were the same throughout the thickness of the strip, the temperature on the side away from the gas would be 1°·1 less than on the exposed side. As a matter of fact, the gradient is less at points within the strip, and it is apparent that there can be no serious difference of

temperature between one part of the section and another. A small deviation from uniformity is without effect, the rise of resistance being, to a first approximation, proportional to the mean temperature across the section.

2. *Determination of Heat Lost to Backing.*

If the temperature of the plane surface of an infinite solid vary according to the equation $\theta = F(t)$, where t is the time, then the Fourier analysis shows that the total amount of heat that has passed into the solid at time t is

$$2\sqrt{\frac{kct}{\pi}}\left\{F(t)-\tfrac{1}{3}t\,F'(t)+\tfrac{1}{5}\frac{t^2}{2\,!}F''(t)-...,\right\},$$

where $F'(t), F''(t)...$, are the derived functions of $F(t)$ and k is the thermal conductivity and c the thermal capacity per unit volume of the solid. In our case the solid is the wood backing, and the temperature θ is that of the copper strip. In consequence of the low thermal conductivity of wood, the temperature changes are confined to parts near the copper, and the backing may be treated as infinitely thick, at any rate for the purpose of finding a correction. The heat accounted for in the copper is $CF(t)$, where C is the thermal capacity of the copper strip per unit area. The heat lost to the backing is to that in the copper in the ratio

$$\frac{2}{C}\sqrt{\frac{kct}{\pi}}\left\{1-\tfrac{1}{3}t\frac{F'(t)}{F(t)}+\tfrac{1}{5}\frac{t^2}{2\,!}\cdot\frac{F''(t)}{F(t)}-...\right\}. \tag{1}$$

The values of $F(t), F'(t)...$, etc., are obtained at once from the curve (B in fig. 4) showing the rise of temperature of the strip in terms of the time. In order to obtain the percentage of heat loss, therefore, it is only necessary to find the constant $\dfrac{2}{C}\sqrt{\dfrac{kc}{\pi}}$ in some particular case in which $F(t)$ and the loss of heat are both known.

For this purpose, that part of the strip which is in the cylindrical surface was placed in series with a fuse of No. 18 copper wire, a storage battery of 100 cells, and the series coils of a ballistic wattmeter. • The suspended coil of the wattmeter, in series with a non-inductive resistance of 8000 ohms, was placed as a shunt across the strip. On closing the switch in the battery circuit, the fuse allowed a current of about 350 ampères to pass for about 1·4 seconds before melting. A photographic record of the current was taken with a quick period galvanometer, and it was found to rise within 1/50 second to 365 ampères, it then fell in the course of 1·1 seconds to 340 ampères. Arcing then commenced at the fuse, and the current rapidly fell, ceasing altogether at 1·4 seconds.

The wattmeter was calibrated in the ordinary way with steady currents. Its period of oscillation was 9·77 seconds. The resistance of the strip was measured in the ordinary way at definite intervals after the current had ceased. From the observations of resistance a curve of cooling was obtained and the resistance immediately after the breaking of the fuse was thus calculated. This correction for cooling was small. A large number of observations gave the following results :—

Work done on strip, as measured by wattmeter ...... 3677 calories
Weight of copper .... 1950 grammes
Rise of temperature of copper .... 17°·2 C.
Heat in copper, 17·2 × 1950 × 0·0935 .... 3135 calories
Heat lost to backing, 3677—3135 .... 542 „

The heat lost under these conditions is, therefore, 17½ per cent. of the heat in the copper. During the passage of the current, work is done on the strip at a nearly uniform rate for 1·1 second, and then at a diminishing rate for another 0·3 second. The heat loss will be very nearly the same as though the temperature had risen at a uniform rate for the whole time. Putting $t = 1·4, F(t) = 17·2, F'(t) = 17·2/1·4, F''(t) = 0$, etc., in the expression (1) above, the expression for the fraction of heat lost in this case becomes

$$\frac{2}{C} \sqrt{\frac{1·4kc}{\pi}} \cdot \frac{2}{3} = 0·175,$$

whence

$$\frac{2}{C} \sqrt{\frac{kc}{\pi}} = 0·22.$$

In calculating the heat loss at different points after the explosion, this value of the constant is assumed, and the values of $F(t), F'(t)...$, etc., are taken from the curve of copper temperature (B in fig. 4). For example, at $t = 1$, $F(t) = 35$ mm., $F'(t) = 7·5$ mm. per second, $F''(t) = -2·8$, and so on, the rest of the terms being unimportant. The percentage of heat loss obtained by substituting these figures in expression (1) is approximately 20 per cent.

The specific heat of the strip was determined by the same ballistic wattmeter method, a weighed quantity of strip being wound on a wooden frame, so that heat loss only takes place to the surrounding air. The rise of temperature produced by blowing a No. 18 copper fuse in series with this strip was 18°·2 C., assuming a temperature coefficient of 0·00428. The corresponding value of the specific heat was 0·0935, deduced from the wattmeter reading. A correction of 2½ per cent. had to be applied to the

temperature rise for the cooling which took place before the resistance could be measured. It should be added that in both ballistic wattmeter measurements the reading was corrected for the fact that the period for which the current passed (1·4 seconds) was comparable with the period of the instrument (9·77 seconds). The correction was applied on the assumption that a constant torque acted on the suspended coil for 1·4 seconds, and it amounted to an addition of 2½ per cent.

It was found that the amount of energy put into the copper during the blowing of a copper wire fuse of given size was remarkably constant, never differing by more than 2 or 3 per cent. from the mean. This method of determining specific heats is, I think, capable of considerable accuracy, and is certainly convenient.

Electric Furnace Reactions under High Gaseous Pressures.

By R. S. HUTTON and J. E. PETAVEL.

(Abstract.)

The paper gives an account of a detailed study of a number of electric furnace reactions. The object in view was to investigate the effect of wide variations in the physical conditions.

The experiments were carried out in an air-tight enclosure and, by analysis and measurement of the gaseous as well as of the solid products, every reaction was followed in detail. A careful measurement of the total energy supplied to the furnace was also made, and the calculated yields per kilowatt hour will be found recorded in the appendix.

Special attention was paid to the effect of the pressure and nature of the gaseous atmosphere in which the reaction was carried out.

The principal processes studied are—the formation of calcium carbide, carborundum, and nitric acid, the direct reduction of alumina by carbon, and the fusion of quartz.

A full description is given of the two pressure furnaces in use, as also of the power plant, gas compressing plant, etc. The power employed in the case of the larger furnace was generally 10 to 15 K.W. The furnaces consist essentially of strong steel enclosures provided with the necessary valves, windows, and insulated electrode holders. Inside these pressure chambers any desired arrangement for arc or resistance heating could be mounted.

The currents used ranged up to 1000 ampères, and special fittings were also provided for very high tensions (25,000 volts). Working pressures up to 3000 lb. per square inch were frequently employed, the apparatus being also suitable for use as a vacuum furnace.

The capacity of the larger enclosure was 20 litres, that of the smaller being about one-tenth of this.

Some preliminary experiments dealt with the electrical constants of carbon and metal arcs in air, hydrogen, carbonic acid, nitrogen, and coal gas, which are compared with similar values under ordinary atmospheric conditions. Tables and curves giving the relation between the E.M.F., current, and length

of the arc are given.   Marked differences are noticeable in the character of the discharge in neutral and oxidising atmospheres.

The effect of pressure upon the rate of oxidation of heated metals is also considered.

The formation of calcium carbide is the first electric furnace reaction to be studied.   A vertical smothered arc was used, the charge for each experiment amounting to about 10 kilogrammes of lime and carbon, an ingot of carbide weighing about 1 kilogramme being produced.

The experiments were carried out in an atmosphere (*a*) of carbon monoxide, (*b*) of coal gas, (*c*) of hydrogen at pressures ranging from 7 to 1700 lb. per square inch absolute.   Among the conclusions arrived at the following may be quoted :—

1. Contrary to the views usually held, the pressure of an atmosphere of carbon monoxide during the reaction does not appreciably decrease the yield.

2. If the carbide is cooled in an atmosphere of carbon monoxide, a back reaction occurs at about the freezing point of the substance.   The effect is, however, limited to the surface of the ingot, and when working on a large scale this does not seriously alter the weight of product obtained.

The fusion of quartz under pressure was next undertaken ; the experiments were carried out in air and in hydrogen at pressures up to 2500 lb. per square inch ; they showed *inter alia* a marked decrease in the vaporisation of the fused product, but no appreciable increase in its fluidity and transparency.

It is generally accepted that carborundum results from interaction of silica vapour and carbon.   The diminished vaporisation of silica, noted above, accounts for the very limited formation of carborundum which occurs under pressure ; the proportion of the amorphous variety was also much lower than is usually the case.

The difficult problem of the direct reduction of alumina by carbon resulted in a lengthy and detailed research.   Briefly stated, the conclusions arrived at are :—

1. That metallic aluminium can be produced by a purely thermal reaction.

2. That the lowest temperature at which this reaction can take place coincides with the melting point of alumina.

3. That the metal is first produced in the form of vapour.

Under ordinary conditions, however, carburisation immediately occurs by the interaction of the metal vapour with the carbon monoxide.   To collect the pure metal, two precautions are found to be necessary : (1) The carbon monoxide must be diluted and removed.   (2) The vaporisation of the metal must be limited by operation under high gaseous pressures.

In certain experiments quoted, a small quantity of aluminium (40—50 grammes) was collected, and the working of the process on a large scale is chiefly a matter of the arrangement and construction of the furnace.

The only gaseous reaction referred to in detail is the formation of oxides of nitrogen. Two distinct series of experiments were carried out: For the first, a high tension (25,000 volt) transformer was employed in conjunction with the smaller furnace. In the second series, a more powerful but lower tension arc discharge was spread out by a mechanical interrupter actuated by a small air turbine placed inside the larger furnace. Both series show an increase of efficiency attributable to pressure.

The paper is illustrated by some figures, and followed by an appendix giving a summary of the numerical results.

On the Effect of High Temperatures on Radium Emanation and its Products.

By WALTER MAKOWER, Assistant Lecturer in Physics; and SIDNEY RUSS, Demonstrator in Physics in the University of Manchester.

1. *The Rate of Decay of Radium Emanation at* 1100° C.

In a previous paper[*] it has been shown that the activity of radium emanation sealed in a quartz tube is temporarily changed by subjecting it for a short time to temperatures between 1000° C. and 1200° C. From the results obtained it seemed probable that this change was not due to any alteration of the emanation itself, but rather to a change of activity of one of the more quickly decaying products of the emanation with which it is in equilibrium. It seemed, however, desirable to put the matter beyond doubt, and, at the suggestion of Professor J. J. Thomson, we have measured the rate of decay of the emanation when kept at a temperature of 1100° C. The experiments indicate that the rate of decay of the emanation is the same under these conditions as at ordinary temperatures, the activity falling to half its original value in 3·88 days. This value is intermediate between that obtained by Curie[†] (3·99 days) and that given by Rutherford and Soddy[‡] (3·71 days).

The method of measurement was the same as that employed in the previous research,[§] and a diagram of the apparatus used is reproduced (fig. 1). In the present experiments, however, greater care was taken to
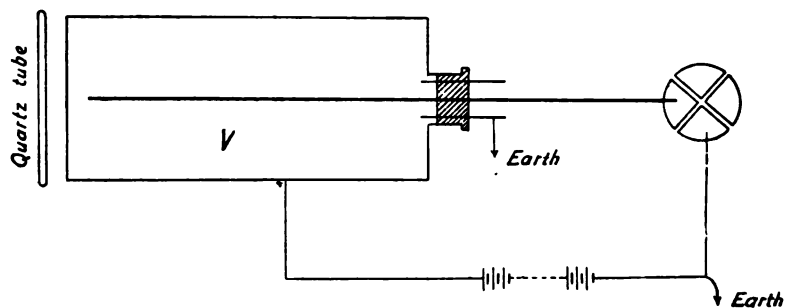

FIG. 1.

* W. Makower, ' Roy. Soc. Proc.,' A, vol. 77, 1906.

† P. Curie, 'Comptes Rendus,' vol. 135, p. 857, 1902.

‡ Rutherford and Soddy, ' Phil. Mag.,' April, 1903.

§ *Loc. cit.*

eliminate errors due to any change of sensitiveness of the electrometer which might have occurred during the 10 days over which the observations extended. For this purpose the ionisation produced in the air contained in a cylindrical vessel by the rays (β and γ) coming from the quartz tube containing the emanation was compared with that produced between two parallel plates by a constant quantity of uranium. Assuming that the radiation from the latter remained constant, it was possible to allow for any slight change of sensitiveness of the electrometer.

A small quartz tube was filled with the emanation from about 5 milligrammes of radium bromide, and then sealed off in the oxyhydrogen blowpipe. After allowing the tube to stand for about six hours for radio-active equilibrium to be established, the activity was measured and the observations repeated at frequent intervals for four days. The tube was then placed in a small nickel wire resistance furnace and kept at 1100° for one hour, after which it was removed for a few minutes, its activity again tested, and found to have fallen about 6 per cent. The tube was then replaced in the furnace, and tested once a day for the next four days by removing from the furnace for as short a time as possible, and measuring in the usual manner. The whole operation could be accomplished in a few minutes, and only very slight errors can have been introduced by allowing the emanation to cool for this short time. On removing the quartz tube from the furnace at the end of the four days' heating, the activity was found to increase for two or three hours, just as when it had been heated only one hour, recovering to the value which it would have reached if it had not been subjected to a high temperature at all. On subsequently heating the quartz tube for a short time, the emanation was found to have retained its property of apparently temporarily changing its activity.

Table I.

Time in hours.	Intensity.	Log intensity.	Time in hours.	Intensity.	Log intensity.
0	185 ·7	2 ·269	118 ·5	72 ·1	1 ·858
13 ·3	157 ·0	2 ·196	139 ·25	58 ·7	1 ·769
24 ·0	140 ·1	2 ·146	163 ·5	50 ·7	1 ·705
36 ·0	135 ·4	2 ·132	187 ·25	41 ·8	1 ·621
40 ·5	134 ·1	2 ·127	187 ·75	43 ·76	1 ·641
48 ·0	117 ·4	2 ·070	188 ·25	43 ·38	1 ·637
61 ·25	114 ·1	2 ·057	190 ·0	43 ·6	1 ·639
67 ·6	109 ·1	2 ·038	208 ·5	37 ·58	1 ·575
72 ·0	107 ·9	2 ·033	214 ·5	36 ·15	1 ·558
84 ·8	88 ·6	1 ·947	228 ·5	32 ·55	1 ·513
92 ·25	94 ·1	1 ·974	229 ·5	30 ·33	1 ·482
93 ·25	83 ·5	1 ·922	256 ·5	26 ·7	1 ·426

. The results are given in full in Table I, and shown graphically in fig. 2, in which the ordinates represent the logarithms of the activity in arbitrary units, and the abscissæ represent time in hours.   It will be seen that the points on the portiou AB of the curve during which the emanation was at
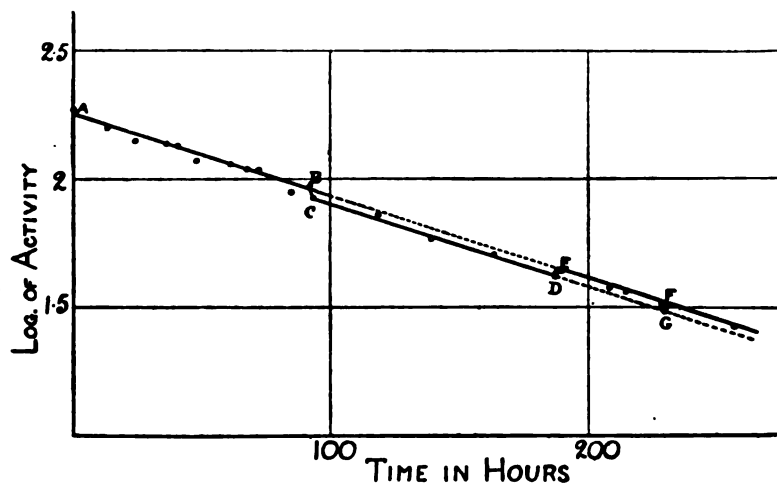
Fig. 2.

atmospheric temperature, lie on a straight line parallel to the portion CD, during which the emanation was at 1100° C.   On allowing the emanation to cool, the subsequent points taken lie on the straight line AB produced.   On again heating for an hour, the point G was obtained, which lies on CD produced.

Since the rate of decay of the emanation is unaltered by high temperature, the change of activity observed when the emanation is heated must be due to some alteration in one of the more rapidly decaying products— A, B, or C.

To decide which of these products was affected by the high temperature, the following experiments were undertaken.

2. *Effect of High Temperature on the Active Deposit from Radium.*

The experiment consisted in collecting on two wires the active deposit from a considerable quantity of radium emanation by immersing the wires simultaneously in the emanation contained in a cylindrical vessel for three or four hours, the wires being situated along the axis of the cylinder.   An electric field was applied between the wires and the vessel, and the wires made the negative electrode, care being taken to expose the wire which was subsequently to be heated to a field of uniform strength.   In this way it was possible to make the wires sufficiently active for the purposes of the experi-

ment. The wires were then removed, and the wire to be heated, which was made of platinum, sealed up in a small quartz tube, and its activity measured before and after heating to a high temperature and compared with the activity of the other wire, which was of steel and which was kept at the ordinary temperature. The heating was not started till at least 20 minutes after removal of the wires from the emanation, so that the quantity of radium A present was negligible.

In the first experiments exactly the same arrangement was used as in the experiments with the emanation. In this way, however, discordant results were obtained, and it was found that the ionisation produced in the testing vessel connected to the electrometer could be varied by rotating the wire on its stand. This change must have been due to a lack of uniformity in the deposit on the wire, so that in some positions the side with the greater concentration of activity was presented to the vessel in which the ionisation was produced, whilst in other positions the side with the less concentration was so placed. As the rays coming from the far side of the wire had to traverse the thickness of the wire before reaching the ionisation vessel, this may well have given rise to the discordant results.

The apparatus was therefore modified, and the following differential method of measuring the change produced by heating the active deposits was found satisfactory. A diagram showing the arrangement finally used is given in fig. 3. A platinum wire, 4 cm. long and 0·3 mm. diameter, was sealed up in a
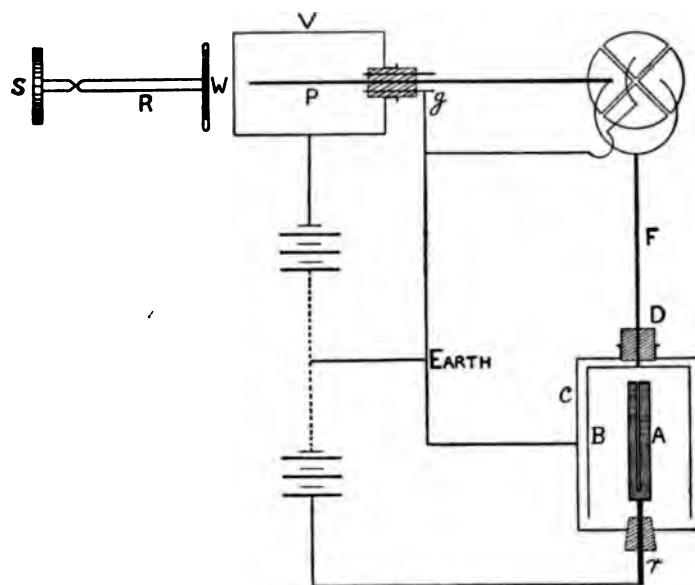

FIG. 3.

small quartz tube just wide enough to take the wire and just long enough to make it possible to seal up the tube without appreciably heating more than a very short length of the wire. The wire was then placed in the wooden tube, A, 6 cm. long, just wide enough to accommodate the quartz tube. The thickness of the walls was 4·5 mm.;* the wooden tube was covered with aluminium leaf, which was in metallic connection with a stout brass rod, *r*, passing through an ebonite plug which served to support the wooden tube. The wooden tube could be placed so as to lie along the axis of a hollow cylindrical metallic vessel, B, closed at one end and enclosed in another outer metallic case, C, connected to earth. Through the ebonite stopper, D, passed a brass rod, F, which was connected to one pair of quadrants of a Dolezalek electrometer, and which served to support the cylinder, B. The saturation current through the air in the space between the wooden tube, A, and the cylinder, B, gave a measure of the activity of the deposit on the platinum wire.

The steel wire, W, was mounted in a glass tube at the end of a rod, R, and at right angles to it. By means of the screw, S, the wire could be brought nearer to the cylindrical metallic vessel, V, or withdrawn from it. Along the axis of V ran a brass rod, P, insulated from it, and connected to the *same* pair of quadrants of the electrometer as B. The other pair of quadrants were permanently connected to earth. The saturation current in V served as a measure of the activity of the wire, W, and the guard ring, *g*, prevented errors due to leakage of electricity from the vessel, V, to the electrometer.

A battery of 300 small accumulators was used to maintain the voltages on *r* and V. The cells were connected in series. The negative pole of the battery being connected to V, the positive to *r*, and the middle cell to earth.

Since the wires, *r* and W, had been exposed to the same emanation for the same time and removed from its influence simultaneously, the activity of both decayed at the same rate. The position of W was so adjusted that the saturation current in V was nearly equal and opposite to the current between A and B. When this had been done, the electrometer showed only a very slight movement when the quadrants were disconnected from earth for one minute. This gave a measure of the *difference* between the saturation currents

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* Wood was selected for this purpose, as its absorption for the rays from the active deposit is relatively small, and the walls could therefore be made thick. In this way the tube could be bored out sufficiently nearly centrally to insure that rays of the same intensity came out uniformly in all directions from the active deposit inside. With steel, which had to be made much thinner to let a measurable quantity of radiation pass through its walls, this was found to be difficult, if not impossible.

in the two vessels. The current through either vessel could also be measured separately. As long as the quartz tube containing the platinum wire remained unheated, the balance was undisturbed, even though the quartz tube was removed and replaced; this point was tested several times in every experiment before heating the quartz tube. But on replacing the quartz tube after heating it to a high temperature the balance was found to have been disturbed, thus showing that the radiation from the platinum wire had been changed. Except in the case of one experiment, No. 5, Table II, *the radiation from the active deposit was less intense than it would have been if the heating had not taken place.* The results obtained are shown in Table II. In

Table II.

Temp. of furnace.	Percentage fall in activity.	Temp. of furnace.	Percentage fall in activity.
° C.		° C.	
700	0	1020	6·2
885	3	1060	8·7
900	8	1080	15·6
935	11	1110	7·9
955	−3	1170	15·4
965	3	1185	14·2
1000	8·5	1250	8·2

each case the quartz tube (or in the case of the lower temperatures, the glass tube) containing the platinum wire on which the active deposit had been collected was kept in the furnace for five minutes. Having tested the activity of the platinum wire after removal from the furnace, observations were continued to see whether the percentage difference of activity between the heated and unheated wire remained constant or not. It was found that this percentage difference always diminished with time when the wire which had been heated was left at the temperature of the room. From this it follows that the activity on the heated wire was decaying at a slower rate than that on the unheated one. The result for one of the above experiments is shown graphically in fig. 4. Curve 1 gives the rate of decay of the unheated deposit on the steel wire; the ordinates represent activity and abscissæ time after removal of wires from the emanation. Curve II gives the rate of decay of the deposit after heating. Curve III has been calculated so as to make the percentage difference between the activity on the two wires constant. It will be noticed that Curves I and II approach each other more rapidly than would be the case if the activity on the two wires were decaying at the same rate.
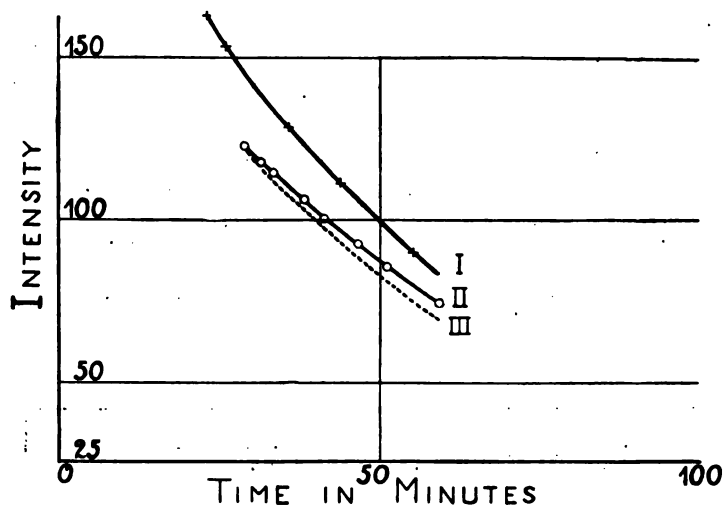
Fig. 4.

Increasing the time for which the active deposit was subjected to the high temperature appeared to be without appreciable effect, the drop in activity being no greater when the time for which the quartz tube was in the furnace was increased from 5 to 15 minutes. In Table III are given the percentage drops in activity under this condition.

Table III.

Temperature C.	Percentage change of activity.
1080°	7·3
1050°	10·0

3. *Discussion of Results.*

The simplest explanation of these phenomena seems to be that radium C undergoes a sudden change when subjected to a high temperature, its activity being thereby diminished. On the other hand, radium B is unaffected by this treatment and continues to supply C at the ordinary rate after removal of the wire from the furnace. The activity of the deposit measured by the β and γ rays (which are emitted by C and not by B) gives a measure of the quantity of C present at any moment and, consequently, if radium C is affected by the high temperature, the sudden change of activity actually observed would be expected. After removal from the furnace the radium C decays and is replaced by a new supply from B, being therefore produced

after removal of the quartz tube from the furnace. The activity on the platinum and steel wires would therefore tend to become more and more nearly equal as time proceeds. This is seen to be the case from the curves given in Fig. 3.

4. *Summary of Results.*

(1) The change in activity noticed when radium emanation is subjected to a high temperature is not due to any alteration in the emanation itself, since its time period is unaltered when it is maintained at a temperature of 1100°.

(2) The change is due *either* to a change in radium B *or* C since the activity of a mixture of these two substances can be changed by heating.

(3) The change is *probably* due to some influence of temperature on radium C. This conclusion is in agreement with the statement made by Curie and Danne.*

We are indebted to the Government Grant Committee for placing a grant at our disposal for the purpose of this research.

[*Note added January* 25, 1907.—Since communicating the above we learn that Dr. Bronson has carried out some interesting experiments on the effect of high temperatures on the activity of radium, which appear at first sight difficult to reconcile with those contained in this paper.

As a result of his experiments, he concludes that there is no change of activity in radium, even when exposed to a temperature of 1600° C., and he also concludes that the change in the activity obtained when radium emanation is heated in a quartz tube and allowed to cool is only apparent; the effect observed he ascribes to a preferential condensation of the active deposit at the ends of the tube used when the latter is removed from the furnace. Now, although this is a possible explanation of the observed phenomena described in the first paper already referred to, yet it seems to be inapplicable to the present experiments, for the quartz tubes in which the active wires were sealed were so small that it is difficult to imagine that any change of distribution of the active deposit due to irregular condensation can have taken place. Moreover, the experiment was so arranged that any such redistribution would have been almost entirely without effect on the results.

We have convinced ourselves of the correctness of this statement by using a wire (sealed in a quartz tube) shorter than that used in the experiments described in this paper, and shifting its position in the cavity of the central electrode. A shift of the wire through half the length of the cavity

* 'Comptes Rendus,' vol. 138, pp. 748—751, March, 1904.

produced only a 12 per cent. change in the ionisation. To account for the observed fall of activity on heating, by assuming a redistribution of the activity, it would therefore be necessary to suppose that the active deposit had been transferred almost completely from one half of the tube to the other, a supposition which seems very unlikely. Moreover, turning the quartz tube upside down in the cavity of the central electrode after heating to 1000° C. gave no sensible change in the ionisation.

There are several important differences between the experiments made by Dr. Bronson and ours. In the first place, Dr. Bronson heated radium itself, whereas we heated the active deposit when separated from radium and the emanation. Although it is difficult to see how this circumstance can have affected the results obtained, yet it is worthy of mention.

A much more important difference lies in the fact that Dr. Bronson measured the activity of the radium while hot, whereas we always allowed the active deposit to cool before making measurements.

Now the activity as measured by the β rays gives a measure of the quantity of radium C present, which in turn depends on the rate at which this product is being produced; and since there appears to be no change in the time constant of any product preceding radium C, the activity as measured by the β rays will be unaltered if time is allowed for equilibrium to be set up between the various products present. The quantity of radium C breaking up in unit time will simply be determined by the rate at which it is being formed, and this, as we have seen, is unaltered. The radiation, as measured by the β rays, will therefore be unaltered, except during the time taken for equilibrium to be established between radium C and the products from which it is being formed, after the change in the time constant, due to heating, has taken place. Since we know nothing about the magnitude of this time, it is quite possible that no change would be detected if the radium were tested while hot, whereas if the radium were first allowed to cool, the change might be detected. It is on this account that we think that the experiments of Dr. Bronson and our own are not necessarily contradictory.]

On the Purification and Testing of Selenion.

By R. THRELFALL, F.R.S.

In 1895 I was enabled by a Royal Society grant to obtain about 100 lbs. weight of selenion of about 99·5-per-cent. selenion content. The grant was applied for to enable me to extend to selenion the investigations already made on purified sulphur.* For the purpose of the investigation it was necessary to purify the selenion beyond the standard usual for material to be used in atomic weight investigations. This proved in the event to be impossible on account of the comparatively slight volatility of selenion dioxide, and the impossibility of preventing its formation in the course of the electric measurements I proposed to carry out. Meanwhile, I had prepared a great deal of very pure selenion, and began to investigate its properties—other than those of conduction, for which absolute purity is essential.†

The method of purification adopted was essentially that of Ekman and Petterson.‡

The operations for the purification, as carried out by these chemists, are as follows :—

1. Solution of crude selenion in nitric acid.

2. Expulsion of excess of acid.

3. Sublimation of selenious oxide.

4. Solution of the sublimate in water and filtration (to get rid of the very insoluble mercury selenite).

. 5. Precipitation of selenion by reduction with hydrochloric acid and sulphur dioxide.

6. Prolonged washing of the precipitated selenion.

7. Reconversion of the selenion into selenious oxide and repeated sublimation in a current of air (to remove possible traces of tellurium).

In addition to a repetition of the above processes, I have investigated the analytical possibilities of the separation of tellurium from selenion, the application of the spectroscope to the testing of selenion for tellurium, the separation of the elements by sublimation of selenion dioxide, and examination of the product.

* Threlfall and Brearley, ' Phil. Trans.,' A, 1896.

† 'Phil. Mag.,' Series 5, p. 42, 1896 ; ' Phys. Review,' vols. 4 and 5, 1897.

‡ " Über das Atomgewicht des Selens," ' Nova Acta der K. Soc. der Wissenschaften zu Upsala,' May 13, 1876, vol. 10, unpaged.

The first step was to investigate the original material for tellurium and, if possible, to find a method of detecting that element in small quantities in presence of selenion. The best of the methods I tried was Oppenheim's.[*] By control experiments it was found that the limits of discrimination lay somewhere between 1/10 per cent. and 1/40 per cent. of tellurium in the selenion—and this only when every precaution is taken. In some trials I used over 40 grammes weight of the original selenion in order to have the advantage of concentration of tellurium. The net result, however, was only to show that there was certainly less than 1/10 per cent. Te, and probably. less than 1/40 per cent. I, therefore, in the first instance, tried to obtain a spectroscopic method of detecting tellurium in presence of selenion, and for that purpose experimented with the electric arc, sparking between carbon terminals kept wet with solutions of tellurous acid and tellurium salts, bunsen flames, etc., but in the end failed to find any line of sufficient persistence to be of service. By mixing 99 parts of very pure selenion with one part of tellurium, I failed to obtain any indication of tellurium, no matter what method I employed.

Attempts were made to separate the dioxides of selenion and tellurium by taking advantage of the great difference of solubility of the oxides; the results for small proportions of tellurium showed that a sharp separation could not be effected in this way.

Attempts to take advantage of the difference in the volatility of the oxides as practised by Ekman and Petterson were more favourable, and the results obtained indicated that a sharp separation could be made by one or at most two sublimations at 360° C.

The method was tested by mixing together 10·0098 grammes of selenion, not specially purified, and 0·09985 gramme of tellurium (bought as pure). This mixture was dissolved in nitric acid, evaporated to dryness as usual, and the residue collected and placed in a platinum boat in a wide glass tube. The tube was kept at a dull red heat, and a stream of dried and filtered air was passed slowly over it. The sublimate was then resublimed at from 290° to 320° C. to a spot further along the tube, and it was found that the resublimation of the first sublimate was complete, showing that nothing had been carried forward mechanically. During this process a trace of red selenion was formed—a thing which Ekman and Petterson have shown is not to be avoided, whatever care in eliminating dust may be taken. The second sublimate was dissolved in water and the solution filtered (though it was practically clear), boiled with hydrochloric acid, saturated with sodium bisulphite and left to stand for 15 hours. The precipitated elements were

* Crookes, 'Select Methods of Chemical Analysis,' 3rd edit., p. 422.

.washed, ground, and rewashed, and finally treated by the Oppenheim method of separation. This showed that no tellurium was present within the limits mentioned. The residue in the boat containing the metallic impurities was treated for the recovery of tellurium, and 0·0975 gramme of tellurium was recovered and weighed. The loss of tellurium from all causes in this rather complicated treatment was therefore 0·00233 gramme. Taking everything into consideration, this loss appeared to be within the limits of the experimental error. The important fact was that the oxide of selenion sublimed at the lowest visible red heat was totally resublimed at a temperature below 320° without any visible residue being left behind. So far as analysis can show, therefore, it appears that sublimation of the oxides affords a method of separation of the elements—though it cannot, of course, be a theoretically perfect method, for the oxide of tellurium must have some vapour pressure at 300° C.

Preparation of Purified Selenion.

Quantities of 335 grammes of bought selenion were treated in each operation.

The material, ground to a fairly fine powder and sieved, was dissolved in nitric acid, the acid removed, and the aqueous solution of selenious acid filtered. The filtrate was evaporated to dryness and the oxide sublimed in dry and dust-free air at 360° C. To effect the sublimation, the oxide of selenion was introduced into a 3-cm. tube in a large platinum boat and sublimation proceeded with till the tube got blocked up. The boat was then withdrawn, and the sublimate washed out of the tube by platinum distilled water. The air was filtered through long tubes containing cotton wool and dried, first by calcium chloride, and then by pure strong sulphuric acid. During the sublimation a certain amount of reduction always took place at first—while traces of water were being given off and an evil-smelling gas (H_2Se ?) was evolved in small quantity. On resubliming a portion of the sublimate, there was no further reduction or evolution of gas.

The sublimed selenion dioxide was dissolved to an almost absolutely clear and colourless solution in platinum distilled water, and this was then filtered and boiled with much water containing one-ninth of its volume of strong hydrochloric acid, and the selenion precipitated at the air temperature by sulphur dioxide which had passed through several wash bottles and finally through a solution of silver nitrate. Sulphur dioxide was at first prepared from copper and sulphuric acid, and though there was no milkiness in the wash bottles or darkening of the precipitated silver sulphite, it was feared that some sulphuretted hydrogen might possibly be formed, and therefore

recourse was had, first to the production of the gas from sodium bisulphite, and finally to its production from the combustion of very pure sulphur. In the latter case rather elaborate arrangements were required. The sulphur was burned in a large sheet-iron cylindrical vessel, provided with a zinc tray containing the sulphur. The gases coming from the chamber passed in order through a glass tube 7 feet long; a plug of glass wool, a Liebig's condenser, Woolfe's bottle containing distilled water, a plug of cotton wool 2 inches long, a tube containing more cotton wool and copper turnings; a tight plug of glass wool (to filter off the dust from the cotton wool if any was produced), and a long tube containing copper and silver foil. The precipitation vessel was closed and communicated with a suction pump, whereby the gases were drawn through the system. Most of the selenion prepared was precipitated by sulphur dioxide, prepared as described.

The operation of precipitating selenion is not complete for some time. The fine red powder of selenion (which is free from lumps or coagulated portions when the precipitation has been carried out without appreciable rise of temperature) was washed on a platinum cone, and then exhibits many of the characteristics of a gelatinous substance—for instance, it could be got to vibrate when distorted, just like a jelly.

The washing is continued till some time after no trace of hydrochloric or sulphuric acid can be detected in the washings. The fine selenion is then coagulated to some extent by starting the filtering pump, which causes it to occupy a much reduced volume, and finally dried in a dish in a water bath, when a great deal of water separates and the selenion coagulates and becomes dark in colour. No HCl or H_2SO_4 could be found in the water which separated.

The drying is continued till the mass can be broken up, when it is again heated in a water oven and finally placed in a vacuum desiccator.

When the selenion appeared to be dry, it was distilled in a current of air residue in a hard glass retort protected by a fireclay and asbestos coating.

The air residue, consisting for the most part of nitrogen, was produced as described in a previous paper.[*]

In spite of all precautions, some oxide of selenion appeared in the receiver, and this was as far as possible caused to deposit on the top of the receiver by keeping the selenion hot, but of course there is no certainty that it was all concentrated there.

An attempt was made to get rid of SeO_2 by redistilling the selenion from bulb to bulb *in vacuo* in a tube blown with three bulbs. The first bulb was charged with some of the distilled selenion which had come over first, the

* 'Phil. Mag.,' Series 5, vol. 35, p. 1, Jan., 1893.

tube was pumped out by a Sprengel pump and filled with the air residue, and was also provided with a piece of metallic magnesium at one end. The magnesium was heated both during pumping and later, when the tube was sealed off. The tube was heated while still in connection with the pump, and as the selenion melted it just gave enough gas to change the sound of the pump, but not enough to examine—it was estimated at less than 1/20 of the volume of the selenion (say 1/10 c.c.). There was sufficient selenion dioxide driven off by heating the selenion to form a visible deposit on the next bulb of the tube. Now the heating may be considered to have taken place under conditions precluding the presence of any appreciable amount of oxygen in the high vacuum attained in presence of hot magnesium, so we must conclude that the selenion, as prepared in bulk, either contains some oxide, or oxidises during removal and storage at ordinary temperatures. Even if it had been practicable to heat all the selenion in a high vacuum, there is no evidence that all the oxide could be separated, and no test can be made to establish with certainty that oxide is absent, even after such treatment (see below). I was therefore obliged to abandon the scheme of treating selenion as a simple elemental body for conductivity experiments.

The selenion, prepared in the manner described above, was tested in the following way—it being recognised that both arsenic and mercury, besides unknown elements, might be present.

Samples of about 10 grammes weight were dissolved in strong nitric acid, the acid evaporated with constant additions of water on the water bath, and the dry selenion dioxide dissolved in water. In all cases the nitric acid solution was absolutely clear and left no residue. The aqueous solution was just visibly opalescent, possibly through a slight reduction of the selenious acid by dust or owing to the presence of mercury selenite.

There appears to be some question as to the reliability of the modern methods of testing for arsenic in presence of selenion.* After some preliminary trials, the following method was adopted.

Ten grammes of selenion were converted into selenious acid and dissolved in water. The solution was mixed with a large excess of a solution of ferrous chloride and distilled in presence of a stream of hydrochloric acid gas bubbled through the apparatus. Water was added till the distillate measured three times the volume of the original mixture put into the retort. The distillates were divided into four portions, of which the first and last were much smaller than the second and third. All distillates were saturated with H_2S with all precautions and filtered. The precipitates (visible or invisible) were dissolved in small quantities of 20-per-cent. solution of pure sodium hydrate, acidified

* Berry, 'Soc. Chem. Ind. Journ.,' 1901, p. 322.

with sulphuric acid, boiled with potassium meta-bisulphite, and used in the electrolytic arsenic apparatus of Dr. Thorpe.*

The first distillate was from the ferrous chloride and hydrochloric acid only, and showed no arsenic, the second and third gave arsenic mirrors, and the fourth no mirror.

The total arsenic collected amounted to 0·05 milligramme As_2O_3 or 0·00038 per cent. arsenic in the material tested.

Check experiments were made to test whether the selenion, in being reduced by the ferrous chloride and hydrochloric acid, prevents arsenic from distilling over, and whether the Thorpe apparatus gives a correct result for a solution of selenide of arsenic when treated as above. The result of these tests was to show that the ferrous chloride distillation is effective in causing the arsenic to pass into the distillate, and that the arsenic is properly shown by the Thorpe apparatus. I have to thank Mr. T. H. Waller for suggesting the distillation with ferrous chloride and hydrochloric acid.

Testing for Mercury.—This is a matter of some difficulty, but the fact that an almost absolutely clear solution of selenious acid was obtained precludes the possibility of the presence of more than very minute quantities. Two methods of testing were employed.

In the first, 10 grammes of selenion were converted into sodium seleniate— or at all events selenious acid was neutralised with sodium hydrate and the product dried. The dry salt was then heated in a tube between plugs . of glass wool to a bright red heat in a current of purified and dried air just sufficient to insure that anything capable of subliming should be carried into the cool part of the tube. The result was a large sublimate of selenious oxide. This sublimate was dissolved in water, saturated with excess of precipitated carbonate of calcium, dried on the water bath, and reheated in a hard glass tube, as before, first to a dull and afterwards to a bright red heat. The cold part of the tube contained a just visible sublimate. Mercury was tested for by Marcel's method,† using one strip of paper saturated with ammoniacal silver nitrate, and another saturated with hydrochloroplatinic acid. The paper saturated with the silver compound did darken as the sublimate was chased up to it by a flame, but the appearance was not that produced by mercury, as shown in a check experiment; the platinum paper was not affected. This is a very sensitive test for mercury as claimed by Marcel.

The second investigation was kindly made for me by Dr. H. Sand, of Nottingham, by means of a rotating cathode which he has studied in regard

* 'Chem. Soc. Trans.,' 1903, vol. 83, p. 969.
† 'Comptes Rend.,' 1873.

to the separation of metals by electrolysis at carefully regulated voltages. About 11 grammes of the purified selenion were converted into selenious acid—acidified with nitric acid and electrolysed under the conditions known to precipitate mercury from other salts—on to the rotating cathode. After an hour's work no deposit could be detected on the cathode, so it was made an anode in a small quantity of dilute nitric acid and a current passed to a fine platinum wire cathode. No mercury was deposited on the fine wire.

The sensitiveness of the method has not been communicated to me by Dr. Sand, but it probably is sensitive enough to show the presence of small quantities of mercury. We may conclude that either there is no mercury in the purified selenion, or if there is it is probably of the order of the arsenic content.

A sample of the selenion which had been used by Messrs. Mason and Vonwiller was returned to me for examination towards the end of 1906, and was examined by solution in nitric acid, etc. Nothing large enough to weigh could be extracted from 10-gramme samples, but there was, nevertheless, evidence that the selenion had picked up some impurities in the varied experiments which had been made upon it. Originally it was some of the purified and distilled product described above. There was a trace of organic matter separable from the nitric-acid solution, and a few specks of insoluble white matter in the aqueous solution of selenious acid. There was also a trace of iron and alumina. The result of treating the filtrate from selenion precipitated by hydrochloric acid and sulphur dioxide with sulphuretted hydrogen was a minute dark-coloured precipitate which was tested in the usual way, but could not, owing to its small quantity, be satisfactorily examined. Special tests for gold and platinum showed that it was not the latter, the former doubtful, and it did not appear to be mercury. Taking all the residues and precipitates together, the total weight could not have been more than 1 or 2 milligrammes. My opinion is that the contamination consisted mainly of dust with a trace of mercury or gold, and some hydrocarbon—possibly oil or paraffin.

In letters of October 30 and November 19, Professor Pollock informs me that the selenion was, in fact, floated on mercury in some of the experiments and gilded in others, and the material had been remelted at least a dozen times, so some contamination was to be expected. I made a special investigation for zinc, as Messrs. Mason and Vonwiller state that the selenion was melted in a zinc vessel, but the material was found absolutely free from this element, at all events to tests by potassium ferrocyanide and sodium sulphide, which are fairly delicate.

A test for SeO_2 was made in the following manner: About 4 grammes of the selenion was placed in a hard glass tube 1 cm. diameter, drawn out to a long point—about 20 cm. long and 2 mm. diameter. The tube was connected with an apparatus for supplying hydrogen absolutely freed from oxygen, and was filled and pumped out many times. Finally, the pressure was reduced to about 30 mm. mercury, and sufficient hydrogen allowed to enter to insure that sublimates would be carried into the narrow part of the tube. A just visible sublimate of SeO_2 was observed. On repeating the trial with the same selenion to which 1 milligramme of SeO_2 had been added, the sublimate was, at least, doubled, and, on adding 4 milligrammes, a comparatively large sublimate was obtained, but it was almost instantly covered over by a deposit of selenion, or was reduced and thus removed. I think it is safe to conclude that 4 grammes of the selenion used by Vonwiller and Mason did not contain anything like 5 milligrammes of SeO_2, and probably only about 1 milligramme; but the test is not entirely satisfactory.

On the Specific Inductive Capacity of a Sample of Highly Purified Selenion.

By O. U. Vonwiller, B.Sc., Demonstrator in Physics, and W. H. Mason, B.Sc., Deas-Thomson Scholar in Physics in the University of Sydney.

(Communicated by R. Threlfall, F.R.S. Received January 18,—Read February 14, 1907.)

General Results of the Measurements.

For the purpose of the electrical measurements, the selenion, purified as described in R. Threlfall's paper, was cast into the form of a circular plate about 15 cm. in diameter and 1 cm. thick. To make the casting, the selenion was heated until thoroughly liquid, which occurred at a temperature between 200° and 230° C., then poured into an open zinc mould previously warmed, and allowed to cool at the air temperature. Under the circumstances the selenion assumed the vitreous form,* the fracture being conchoidal and the specific gravity 4·29 at 13°·8 C. When hard, the end surfaces of the plate were carefully ground flat and parallel to each other, the grinding being done with carborundum powder. After the completion of each set of measurements the plate was broken into small pieces to ascertain if the material was homogeneous throughout; on no occasion were any air bubbles found which could in any way affect the accuracy of the measurements.

Determinations of the specific inductive capacity of the selenion forming the plate so prepared were made by the absolute electrometer method, with alternating electric forces having a frequency of about 50 per second; and by a method using electric oscillations with a frequency of 24,000,000 per second. Table I gives the results obtained, the measurements being made with the selenion in the dark.

The investigation shows that to the order of the accuracy of the measurements for the sample of selenion tested, the specific inductive capacity is the same under alternating electrical forces having a frequency of 24,000,000 per second, as it is under forces whose frequency is only 50 per second.

This result for the sample of selenion is similar to that found for the specimen of glass examined by the same methods as those described in this paper by Pollock and Vonwiller.†

* Saunders, 'Journ. Phys. Chem.,' vol. 4, 1900.
† 'Phil. Mag.,' June, 1902.

Table I.—Values of Specific Inductive Capacity.

By electrometer method.		By electrical oscillation method.	
Temp. ° C.	K.	Temp. ° C.	K.
12 ·5	6 ·20	23 ·0	6 ·09
12 ·5	6 ·07	24 ·1	6 ·16
19 ·3	6 ·09	23 ·7	6 ·16
19 ·8	6 ·17	—	—
Means ... 16 ·0	6 ·13	23 ·6	6 ·14

For the plate of selenion used in the final determination of the specific inductive capacity by the electrometer method, the specific resistance with the selenion in the dark was found to be $2·2 \times 10^{16}$ ohms at 20° C. and $6·5 \times 10^{15}$ ohms at 25° C.; these values are to be considered provisional only, more exact determinations extending over a wider range of temperature are now in progress. The specific resistance decreased considerably when the selenion was exposed to light. The comparatively high conductivity imparted to the plate by the very thin reddish film which forms on surfaces of vitreous selenion, though only exposed to air, gave considerable trouble until its cause was discovered. For all measurements it was found necessary to first remove this film by the careful use of glass paper.

The specific gravity of the material was found by weighing, in air and in water, a whole plate and a fragment after the plate was broken up; the results are identical, giving 4·29 as the value of the specific gravity at 13°·8 and 16°·2 C.

In the report of the Melbourne Meeting of the Australasian Association for the Advancement of Science (1900), Madsen published values of the specific inductive capacity of selenion obtained from measurements with the same sample of selenion as that used in the present determination, but with a different form of absolute electrometer. The mean value given is 5·74; we are, however, satisfied that some source of constant error remained undetected in the measurements, and that the values given are considerably too low.

V. Pirani* measured the specific inductive capacity of commercial selenion and obtained values between 7·4 and 7·58. Sufficient data are not given to enable us to estimate the degree of accuracy attained in this measurement.

* Inaugural Dissertation, Berlin, 1903.

Measurement of the Specific Inductive Capacity by the Absolute Electrometer Method.

The apparatus used was that employed by Pollock and Vonwiller in measuring the specific inductive capacity of a specimen of glass, and fully described by them,* the only change being the substitution for the central swinging brass plate of an aluminium plate of similar dimensions, the lower surface being scraped truly plane; this enables the value of the electrostatic pull to be determined with slightly increased accuracy.

The results are given in Table II, where the overload represents the mass in grammes whose weight counterbalances the electrostatic pull.

Table II.—Results of Absolute Electrometer Method.

Date.	Potential difference.	Distance between plates.	Thickness of selenion.	Overload.		Temp. °C.	K.
				Without selenion.	With selenion.		
	volts.	cm.	cm.	gramme.	gramme.		
August 11, 1904	4420	2·168	0·880	0·104	0·240	12·5	6·20
,, ,,	4470	2·168	0·880	0·107	0·245	12·5	6·07
May 26, 1905......	2820	1·507	0·858	0·102	0·371	19·3	6·09
May 29, 1905......	5000	1·505	0·858	0·296	1·085	19·8	6·17

Mean value of K...... 6·13 at 16°·0 C.

Measurement of the Specific Inductive Capacity with High Frequency Alternating Electric Forces.

The method used was that employed by one of us in observing the variation in the dielectric constant of water at low temperatures.† The arrangement of the apparatus is shown in fig. 1.   Electrical oscillations were
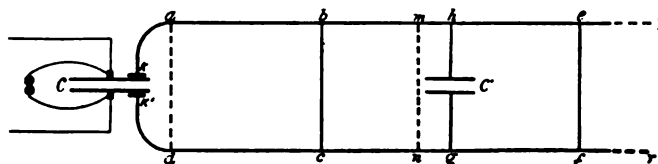

Fig. 1

set up in the two wire circuits *kbck'* (the primary) and *befc* (the secondary) by the oscillatory discharge of the condenser C; Rutherford solenoidal magnetic detectors being placed in the two circuits, and the primary arranged

* 'Phil. Mag.,' June, 1902.
† Vonwiller, 'Phil. Mag.,' June, 1904.

to be in tune with the condenser vibration. The dimensions of the secondary circuit and the capacity of the condenser C′ were chosen as described in the former paper, so that the maximum variation in the demagnetisation of the Rutherford detector in the secondary, was obtained for a given percentage change in the capacity of the condenser C′. This condenser consisted of two parallel circular brass plates 10·4 cm. in diameter and 0·237 cm. thick whose distance apart could be altered. The lengths *bh*, *he*, were each made 200 cm. (altered to 215 and 205 cm. in the second and third experiments, Table III), and as the plates of C′ were moved apart, deflections produced by the two detectors were observed for each position. In fig. 2 is shown the variation of the secondary deflection (corrected to a
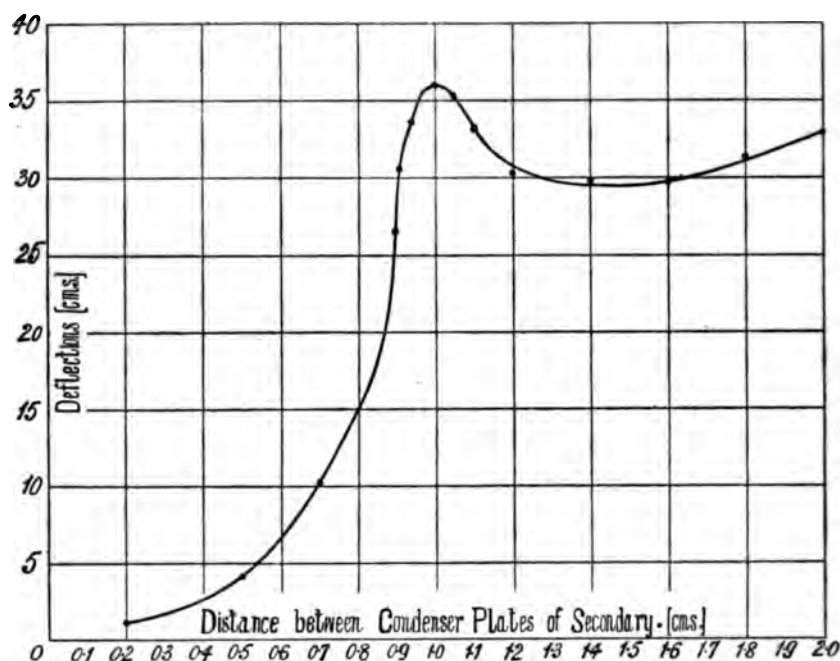
Fɪɢ. 2.

standard primary deflection) as the distance between the plates is changed: an inspection of the figure shows that a position of high sensitiveness is obtained when the plates are about 9 mm. apart. The capacity in this position was calculated by Kirchhoff's formula*

$$C = \frac{r^2}{4a} + \frac{r}{4\pi a}\left[-a + a \log\frac{16\pi r(a+d)}{a^2} + d\log\frac{a+d}{d}\right],$$

r being the radius of the plates, *d* their thickness, and *a* their distance apart.

* 'Abhandl.,' p. 112.

If a plate of a dielectric of radius r_1 less than r and thickness a_1 is placed between the plates of the condenser (the condenser plates touching the dielectric) the capacity, if a_1 is less than $\frac{1}{4}r$, is

$$C = \frac{Kr_1^2}{4a_1} + \frac{r^2 - r_1^2}{4a_1} + \frac{r}{4\pi a_1}\left[-a_1 + a_1 \log \frac{16\pi r(a_1 + d)}{a_1^2} + d \log \frac{a_1 + d}{d}\right],$$

K being the specific inductive capacity of the dielectric.

A preliminary calculation, assuming K to be the same as at low frequencies, gave dimensions for the selenion plate which would give the same capacity as was obtained when the plates were about 9 mm. apart, with air as the dielectric, and also satisfy the conditions that a should be less than $\frac{1}{4}r$ and that r_1 should be not much less than about $\frac{3}{4}r$, the sensitiveness of the test being decreased as r_1 is decreased, owing to the part of the capacity due to the selenion becoming small in comparison with the whole.

A plate of selenion of suitable dimensions was then prepared in the manner already described and placed between the condenser plates and a number of deflections of both detectors observed, single sparks being used and the mean ratio of the two deflections determined. The selenion was then removed and the plates approached until two positions were obtained, for one of which the ratio of the deflections was slightly above, and for the other slightly below, that obtained with the selenion, the correct position being obtained by interpolation. The results of the observations are given in Table III.

Table III.—Results of Electric Oscillation Method.

Date.	Dielectric between plates.	Deflection of secondary detector.	Distance between plates of C'.	Radius of plate of selenion.	Length, $b-e$, fig. 1.	Temp. °C.	K.
		cm.	cm.	cm.	cm.		
December 15, 1904	Selenion	30·5	2·543	3·190	400 ⎫	23·0	6·09
„ „	Air	30·5	0·937	—	400 ⎬		
January 31, 1905	Selenion	16·4	2·535	3·187	430 ⎫	24·1	6·16
„ „	Air	16·4	0·928	—	430 ⎬		
February 2, 1905	Selenion	23·9	2·535	3·187	410 ⎫	23·7	6·16
„ „	Air	23·9	0·9275	—	410 ⎬		

Mean value of K...... 6·14 at 23°·6 C.

In order to make absolutely certain that when the selenion was between the plates the readings corresponded to those obtained with air between the plates at a distance apart of about 9·3 mm., and not 11 or 20 mm., where the deflections would have the same value (see fig. 2), readings were taken with

one of the condenser plates not touching the selenion, but with a small thickness of glass or mica between, the capacity being thus reduced.

It was found then that the deflections were increased, indicating a nearer approach to resonance, as was to be expected, and the rate of increase was such as to indicate that the position corresponded to that with air between the plates at a distance apart of about 9 mm. rather than 20 mm., where the deflections would also increase with a decrease of capacity.

The frequency of the electric oscillations set up in the system was determined with sufficient accuracy from the dimensions of the secondary circuit when in tune with the primary.   W. B. Morton* gives, then,

$$\cot \frac{2\pi x}{\lambda} + \cot \frac{2\pi y}{\lambda} = \frac{2\pi}{\lambda} \frac{C}{s},$$

where x is the distance from the centre of the bridge bc to C', y that from the centre of ef to C', C the capacity of C' when the two circuits are in tune, s the capacity per unit length of the parallel wires, and λ the wave-length of the electric oscillations (see fig. 1).   From fig. 2 it is seen that the position of maximum resonance occurs when the plates are 1 cm. apart, C being then 8·9, as s is equal to $(4 \log d/r)^{-1}$, d being the distance between the wires (30 cm.) and r the radius of the wire (0·021 cm.), $s = 1/29\cdot1$; $x = y = 200$ cm., hence λ is found to be 1260 and the frequency about 24,000,000.

Measurement of the Resistance of the Selenion Plate.

Considerable difficulty has been experienced in determining the resistance of the selenion plate.   For the measurement of the resistance to have direct connection with the measurements of the specific inductive capacity, it was essential to employ one of the plates actually used in the experiments to determine the latter constant, and this prevented the selenion being cast into a plate of more suitable form for the resistance measurements.   After some trials, it was found that good contact with the surfaces of the selenion plate could be obtained by coating them with gold leaf and lightly pressing brass plates against the gilt surfaces.   A direct deflection method with a sensitive galvanometer and a voltage of 900 gave no current that could be detected, indicating a specific resistance greater than 10^{14} ohms at $13°·7$ C.; finally the method shown diagrammatically in fig. 3 was adopted.   Here R represents the selenion plate whose resistance is being measured, and r a resistance of about 1000 megohms (determined accurately by a direct deflection method), consisting of a capillary U tube containing alcohol, with platinum wires sealed in at the ends making contact with the liquid.   These resistances were

* 'Phil. Mag.,' May, 1897.

connected to one pair of quadrants of a Dolezalek electrometer, the other pair being earthed; the other terminal of R was joined to the positive pole of a battery of accumulators of which the negative pole was earthed, while the other terminal of r was connected as shown to a potentiometer, the ends of
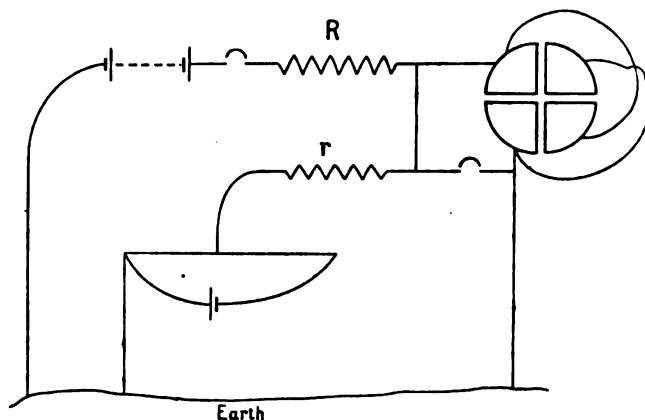

Fig. 3.

which were joined to the poles of a single accumulator, the positive being earthed. The E.M.F. between earth and the end of r, joined to the potentiometer, was varied until the potentials of both pairs of quadrants were the same; if this E.M.F. is e and that of the battery joined to the selenion is E, $e/E = r/R$.

Instead of altering e, the end of r joined to the potentiometer was sometimes earthed and the difference of potential between the quadrants determined by observing the steady deflection of the needle (the instrument having been previously calibrated by means of the potentiometer); if this difference of potential is e, we have $e/E = r/R$, e being extremely small compared with E.

By this method the resistance of a plate 14·636 cm. in diameter and 0·858 cm. thick, was found to be 11×10^{13} ohms at 20° C. and $3·3 \times 10^{13}$ ohms at 25° C., the values of the specific resistance at these temperatures being, therefore, $2·2 \times 10^{16}$ ohms and $6·5 \times 10^{15}$ ohms respectively.

The value of E in different trials varied from 250 to 600 volts; e varied from 3×10^{-3} to 9×10^{-3} volt; as the maximum sensitiveness obtained was a deflection of 1 mm. for 4×10^{-4} volt, a very high degree of accuracy could not be obtained with a plate of the above dimensions.

The measurements described in this paper were made in the Physical Laboratory of the University of Sydney.

On the Theory of Correlation for any Number of Variables, treated by a New System of Notation.

By G. UDNY YULE, Newmarch Lecturer on Statistics, University College, London.

1. The systems of notation hitherto used by writers on the theory of correlation are somewhat unsatisfactory when many variables are involved. In the present paper a new notation is proposed which is simple, definite, and quite general, thus very greatly facilitating the treatment of the subject. The majority of the results given in the sequel were, in fact, first suggested by the notation itself.

2. Let $x_1 x_2 \ldots x_n$ denote deviations in the values of the n variables from their respective arithmetic means. Then the regression equation may be written :—

$$x_1 = b_{12 \cdot 34 \ldots n} x_2 + b_{13 \cdot 24 \ldots n} x_3 + \ldots + b_{1n \cdot 23 \ldots n-1} x_n. \tag{1}$$

In this notation the suffix of each regression coefficient completely defines it. The first subscript gives the dependent variable, the second the variable of which the given regression is the coefficient, and the subscripts after the period show the remaining independent variables which enter into the equation. It is convenient to distinguish the subscripts before and after the period as " primary " and " secondary " subscripts respectively. The order in which the secondary subscripts are arranged is indifferent, but the order of the two primary subscripts is material; e.g., $b_{12 \cdot 3 \ldots n}$ and $b_{21 \cdot 3 \ldots n}$ denote two quite distinct coefficients. A coefficient with p secondary subscripts may be termed a regression of the pth order, the total regressions b_{12}, b_{13}, b_{23}, etc., being thus regarded as of order zero.

3. The correlation-coefficients may be distinguished by subscripts in precisely the same manner. Thus the correlation $r_{12 \cdot 34 \ldots n}$ is defined by the relation

$$r_{12 \cdot 34 \ldots n} = (b_{12 \cdot 34 \ldots n} \cdot b_{21 \cdot 34 \ldots n})^{\frac{1}{2}}. \tag{2}$$

In the case of the correlations, the order of both primary and secondary subscripts is indifferent. A correlation with p secondary subscripts may be termed a correlation of order p, the total correlations r_{12}, r_{13}, r_{23}, etc., being regarded as of order zero.

4. If the regressions in equation (1) be determined as usual by the method

of least squares, the difference between x_1 and the expression on the right, for any observed set of values of $x_1 x_2 .. x_n$, may be denoted by $x_{1.23...n}$: that is

$$x_{1.23...n} = x_1 - b_{12.34...n} x_2 - b_{13.34...n} x_3 - ... - b_{1n.23...n-1} x_n. \qquad (3)$$

Such a residual, or deviation, denoted by a symbol with p secondary subscripts may be termed a deviation of the pth order, $x_1 x_2 .. x_n$ being regarded as deviations of order zero.

5. Finally, the standard deviation $\sigma_{1.23...n}$ is defined as given by the relation

$$N . \sigma^2_{1.23...n} = \Sigma (x^2_{1.23...n}), \qquad (4)$$

N being the number of observations. If the standard deviation be denoted by a symbol with p secondary subscripts, it is of the pth order, the total standard deviations being regarded as of order zero.

6. In terms of this notation, the normal equations from which the regressions are determined may be very briefly written, in the form

$$\Sigma (x_2 . x_{1.23...n}) = \Sigma (x_3 . x_{1.23...n}) = ...$$
$$= \Sigma (x_n . x_{1.23...n}) = 0. \qquad (5)$$

That is to say, we have the general theorem: "The product-sum of any deviation of order zero with any deviation of higher order is zero, provided the subscript of the former occur amongst the secondary subscripts of the latter."

7. It follows that the product-sum of any two deviations of the same order, with the same secondary suffixes, is unaltered by omitting any or all of the secondary subscripts of either and, conversely, the product-sum of any deviation of order p with a deviation of order $p+q$, the p subscripts being the same in each case, is unaltered by adding to the secondary subscripts of the former any or all of the q additional subscripts of the latter, for we have by § 6 :—

$$\Sigma (x_{1.34...n} x_{2.34...n}) = \Sigma (x_{1.34...n}) (x_2 - b_{23.4...n} x_3 - ... - b_{2n.3...n-1} x_n)$$
$$= \Sigma (x_{1.34...n} x_2).$$

Similarly

$$\Sigma (x_{1.34...n} x_{2.34...n-1}) = \Sigma (x_{1.34...n} x_2),$$

and so on. Therefore, quite generally,

$$\Sigma (x_{1.34...n} x_{2.34...n}) = \Sigma (x_{1.34...n} x_{2.34...n-1}) = ...$$
$$... = \Sigma (x_{1.34...n} x_2). \qquad (6)$$

8. It follows from § 7 as a corollary from § 6 that the product-sum of any two deviations is zero if all the subscripts of the one are contained among the secondary subscripts of the other.

These theorems (§§ 6—8) give the key to simple deductions of many results in the theory of multiple correlation.

9. We have from the last section and § 7,

$$0 = \Sigma \left(x_{2\cdot34\dots n} x_{1\cdot234\dots n} \right)$$

$$= \Sigma \left(x_{2\cdot34\dots n} \right) \left(x_1 - b_{12\cdot34\dots n} x_2 - \text{terms in } x_3 \text{ to } x_n \right)$$

$$= \Sigma \left(x_1 x_{2\cdot34\dots n} \right) - b_{12\cdot34\dots n} \Sigma \left(x_2 x_{2\cdot34\dots n} \right)$$

$$= \Sigma \left(x_{1\cdot34\dots n} x_{2\cdot34\dots n} \right) - b_{12\cdot34\dots n} \Sigma \left(x^2_{2\cdot34\dots n} \right).$$

That is

$$b_{12\cdot34\dots n} = \frac{\Sigma \left(x_{1\cdot34\dots n} x_{2\cdot34\dots n} \right)}{\Sigma \left(x^2_{2\cdot34\dots n} \right)}. \tag{7}$$

But this is the value that would have been obtained by taking a regression equation of the form

$$x_{1\cdot34\dots n} = b_{12\cdot34\dots n} x_{2\cdot34\dots n},$$

and determining $b_{12\cdot34\dots n}$ by the method of least squares. That is to say, $b_{12\cdot34\dots n}$ may be regarded, quite generally and without any reference to the form of the frequency distribution, as the regression of $x_{1\cdot34\dots n}$ on $x_{2\cdot34\dots n}$. It follows at once from the definition (3) that $r_{12\cdot34\dots n}$ may be regarded as the correlation between $x_{1\cdot34\dots n}$ and $x_{2\cdot34\dots n}$, and from (4) that we may write

$$b_{12\cdot34\dots n} = r_{12\cdot34\dots n} \frac{\sigma_{1\cdot34\dots n}}{\sigma_{2\cdot34\dots n}}. \tag{8}$$

All the relations, in fact, that hold good between deviation-sums, standard deviations, regressions and correlations of order zero, are also valid between deviation-sums, standard deviations, regressions and correlations of any high order.

10. This result is of some importance as regards the interpretation of partial correlations and regressions. In the case of normal correlation there is no difficulty in assigning a meaning to these constants, as the regression is strictly linear, and the partial correlations and regressions are the same for all types of the variables. But in the general case this is not so, and although I showed, in a previous discussion of the question,[*] that the values assigned to the partial regressions on the assumption of normal correlation are the " least square " values and, consequently, that the partial correlation retains an " average significance," I could not prove that it remains an actual correlation between determinate variables. The above theorem completes the work in this respect. If, with three variables x_1, x_2, and x_3, for example, the two regressions b_{13} and b_{23} be determined in the ordinary way, and then the residuals $x_{1\cdot3} = x_1 - b_{13}x_3$, $x_{2\cdot3} = x_2 - b_{23}x_3$ be calculated for all sets of observations $x'_1 x'_2 x'_3$, $x''_1 x''_2 x''_3$, etc., the correlation between $x_{1\cdot3}$ and $x_{2\cdot3}$ is $r_{12\cdot3}$. A similar interpretation holds for any greater number of variables.

* 'Roy. Soc. Proc.,' vol. 60 (1897), p. 477 ; 'Roy. Stat. Soc. Journ.,' vol. 60 (1897), p. 812.

Such a relation would not, of course, afford a practical method of calculating the partial coefficients, as the arithmetic would be extremely lengthy.

11. Any standard deviation of order p may be expressed in terms of a standard deviation of order $p-1$ and a correlation of order $p-1$. For we have, using the theorems of §§ 6 and 7,

$$\Sigma\left(x^2_{1.23\ldots n}\right) = \Sigma\left(x_{1.23\ldots n-1}x_{1.23\ldots n}\right)$$

$$= \Sigma\left(x_{1.23\ldots n-1}\right)\left(x_1-b_{1n.23\ldots n-1}x_n-\text{terms in } x_2 \text{ to } x_{n-1}\right)$$

$$= \Sigma\left(x^2_{1.23\ldots n-1}\right)-b_{1n.23\ldots n-1}\Sigma\left(x_{1.23\ldots n-1}x_{n.23\ldots n-1}\right);$$

or, dividing through by the number of observations,

$$\sigma^2_{1.23\ldots n} = \sigma^2_{1.23\ldots n-1}\left(1-b_{1n.23\ldots n-1}b_{n1.23\ldots n-1}\right)$$

$$= \sigma^2_{1.23\ldots n-1}\left(1-r^2_{1n.23\ldots n-1}\right). \tag{9}$$

The form of this relation is the same as that of the familiar relation between a standard deviation of the first order and a standard deviation of order zero, with the secondary subscripts $_{23\ldots n-1}$ added throughout. It is clear from (9) that $r_{1n.23\ldots n-1}$ cannot be numerically greater than unity. It also follows at once that if we have been estimating x_1 from $x_2, x_3 \ldots x_{n-1}, x_n$ will not increase the accuracy of estimate unless $r_{1n.23\ldots n-1}$ (not r_{1n}) differ from zero.[*]

12. In equation (9) the subscript n is eliminated from the suffix of $\sigma_{1.23\ldots n}$, and it is obvious that any other subscript can be eliminated in the same way. Therefore we must have

$$\sigma^2_{1.34\ldots n}\left(1-r^2_{12.34\ldots n}\right) = \sigma^2_{1.24\ldots n}\left(1-r^2_{13.24\ldots n}\right)$$

$$= \ldots = \sigma^2_{1.23\ldots n-1}\left(1-r^2_{1n.23\ldots n-1}\right). \tag{10}$$

Further, we have

$$\sigma^2_{1.23\ldots n-1} = \sigma^2_{1.23\ldots n-2}\left(1-r^2_{1(n-1).23\ldots n-2}\right)$$

$$\sigma^2_{1.23\ldots n-2} = \sigma^2_{1.23\ldots n-3}\left(1-r^2_{1(n-2).23\ldots n-3}\right),$$

and so on; so that

$$\sigma^2_{1.23\ldots n} = \sigma^2_1\left(1-r^2_{12}\right)\left(1-r^2_{13.2}\right)\left(1-r^2_{14.23}\right)\ldots\left(1-r^2_{1n.23\ldots n-1}\right). \tag{11}$$

This is an extremely convenient expression for arithmetical use, as illustrated later. A complete check on the arithmetic is obtained by eliminating the secondary subscripts in a different, say the inverse, order, *i.e.*, by using the result—

$$\sigma^2_{1.23\ldots n} = \sigma^2_1\left(1-r^2_{1n}\right)\left(1-r^2_{1(n-1).n}\right)\left(1-r^2_{1(n-2).n(n-1)}\right)\ldots\left(1-r^2_{12.34\ldots n}\right). \tag{12}$$

[*] *Cf.* proofs for cases of 3 and 4 variables previously given (*loc. cit.* in previous note).

13. Any regression of order p may be expressed in terms of regressions of order $p - 1$. For we have

$$\Sigma(x_{1.34\cdots n}x_{2.34\cdots n}) = \Sigma(x_{1.34\cdots n-1}x'_{2.34\cdots n})$$

$$= \Sigma(x_{1.34\cdots n-1})(x_2 - b_{2n.34\cdots n-1}x_n - \text{terms in } x_3 \text{ to } x_{n-1})$$

$$= \Sigma(x_{1.34\cdots n-1}x_{2.34\cdots n-1}) - b_{2n.34\cdots n-1}\Sigma(x_{1.34\cdots n-1}x_{n.34\cdots n-1}).$$

That is, replacing $b_{2n.34\cdots n-1}$ by $b_{n2.34\cdots n-1} \times \sigma^2_{2.34\cdots n-1}/\sigma^2_{n.34\cdots n-1}$,

$$b_{12.34\cdots n}\sigma^2_{2.34\cdots n} = b_{12.34\cdots n-1}\sigma^2_{2.34\cdots n-1} - b_{1n.34\cdots n-1}b_{n2.34\cdots n-1}\sigma^2_{2.34\cdots n-1}.$$

Therefore, by equation (9),

$$b_{12.34\cdots n} = \frac{b_{12.34\cdots n-1} - b_{1n.34\cdots n-1} \cdot b_{n2.34\cdots n-1}}{1 - b_{1n.34\cdots n-1}b_{n1.34\cdots n-1}}. \tag{13}$$

But this is simply the expression for $b_{12.n}$ in terms of b_{12}, b_{1n}, b_{n1}, and b_{n2}, with the subscripts $_{34\cdots n-1}$ added throughout. Therefore $b_{12.34\cdots n}$ may be regarded as the partial regression of $x_{1.34\cdots n-1}$ on $x_{2.34\cdots n-1}$, $x_{n.34\cdots n-1}$ being given. As any other secondary subscript might have been eliminated in lieu of n, we can also regard it as the partial regression of $x_{1.45\cdots n}$, on $x_{2.45\cdots n}$, $x_{3.45\cdots n}$ being given, and so on.

14. Equation (13) may be written in terms of the correlations:—

$$b_{12.34\cdots n} = \frac{r_{12.34\cdots n-1} - r_{1n.34\cdots n-1}r_{2n.34\cdots n-1}}{1 - r^2_{1n.34\cdots n-1}} \frac{\sigma_{1.34\cdots n-1}}{\sigma_{2.34\cdots n-1}}.$$

Hence, writing down the similar expression for $b_{21.34\cdots n}$, and taking the square root of the product,

$$r_{12.34\cdots n} = \frac{r_{12.34\cdots n-1} - r_{1n.34\cdots n-1}r_{2n.34\cdots n-1}}{(1 - r^2_{1n.34\cdots n-1})^{\frac{1}{2}}(1 - r^2_{2n.34\cdots n-1})^{\frac{1}{2}}}. \tag{14}$$

This is, similarly, the expression for $r_{12.n}$ in terms of r_{12}, r_{1n}, and r_{2n}, with the secondary subscripts $_{34\cdots n-1}$ added throughout, and accordingly $r_{12.34\cdots n}$ may be regarded as the partial correlation between $x_{1.34\cdots n-1}$ and $x_{2.34\cdots n-1}$, $x_{n.34\cdots n-1}$ being given, and so on, as for the regression.

15. It is clear that equations (13) and (14) imply a series of relations between correlations or regressions of orders less than $n - 2$ with n variables, for all the expressions obtained by eliminating $_{34\cdots n}$ in turn from the secondary subscripts of the constant on the left must be equal to each other. Further, every coefficient of the pth order can be expressed in terms of the coefficients of the $(p - 1)$th order in p different ways, by eliminating each of the p secondary subscripts in turn. This enables an absolute check to be kept on the arithmetic by calculating each coefficient in at least two distinct ways.

16. By the use of equation (14), the work of calculating correlation coefficients of higher orders is rendered quite simple and straightforward. The use of equation (13) for calculating the regressions is comparatively

clumsy, however: when the correlations have been found, it is best to work out the standard deviations by equation (11), and then the regressions are given at once by (8). The following data, taken from a discussion of pauperism,* will serve as an arithmetical illustration, the variables being the percentage changes during a decade in the poor-law unions of England in: (1) the percentage of the population in receipt of poor-law relief; (2) the ratio of the numbers given relief out-doors to one indoors (in the workhouse); (3) the proportion of aged (over 60) in the population; (4) the population itself. The values of the correlations of order zero are given in Table I, and the logarithms of $(1 - r^2)^{\frac{1}{2}}$, required in the calculations, are entered in the third column. These coefficients are next grouped in sets of three, one set to each possible group of three variables, as in the second column of Table II, and the coefficients of the first order are then calculated from (14). For convenience in calculating the coefficients of the second order, the values of $\log (1 - r^2)^{\frac{1}{2}}$ are again entered in the last column.

Table I.

Correlation coefficient.		$\log \sqrt{1-r^2}$.
12	+0 ·52	1 ·93154
13	+0 ·41	1 ·96003
14	−0 ·14	1 ·99570
23	+0 ·49	1 ·94038
24	+0 ·23	1 ·98820
34	+0 ·25	1 ·98598

Table II.

Correlation coefficient (zero order).		Product term of numerator.	Numerator.	Correlation coefficient (first order).		$\log \sqrt{1-r^2}$.
12	+0 ·52	+0 ·2009	+0 ·3191	12 ·3	+0 ·4014	1 ·92370
13	+0 ·41	+0 ·2548	+0 ·1552	13 ·2	+0 ·2084	1 ·98071
23	+0 ·49	+0 ·2132	+0 ·2768	23 ·1	+0 ·3558	1 ·94139
12	+0 ·52	−0 ·0322	+0 ·5522	12 ·4	+0 ·5731	1 ·82709
14	−0 ·14	+0 ·1196	−0 ·2596	14 ·2	−0 ·3123	1 ·95544
24	+0 ·23	−0 ·0728	+0 ·3028	24 ·1	+0 ·3580	1 ·94044
13	+0 ·41	−0 ·0350	+0 ·4450	13 ·4	+0 ·4642	1 ·89460
14	−0 ·14	+0 ·1025	−0 ·2425	14 ·3	−0 ·2746	1 ·96595
34	+0 ·25	−0 ·0574	+0 ·3074	34 ·1	+0 ·3404	1 ·94652
23	+0 ·49	+0 ·0575	+0 ·4325	23 ·4	+0 ·4590	1 ·89726
24	+0 ·23	+0 ·1225	+0 ·1075	24 ·3	+0 ·1274	1 ·99290
34	+0 ·25	+0 ·1127	+0 ·1373	34 ·2	+0 ·1618	1 ·98848

* 'Roy. Stat. Soc. Journ.,' vol. 62 (1899), p. 249.

Table III.

Correlation coefficient (first order).		Product term of numerator.	Numerator.	Correlation coefficient (second order).		log $\sqrt{1-r^2}$.
12·4	+0·5731	+0·2181	+0·3600	12·34	+0·458	1·89774
13·4	+0·4642	+0·2630	+0·2012	13·24	+0·276	1·96559
23·4	+0·4590	+0·2660	+0·1930	23·14	+0·266	1·96814
12·3	+0·4014	−0·0350	+0·4364	12·34	+0·458	—
14·3	−0·2746	+0·0511	−0·3257	14·23	−0·359	1·94007
24·3	+0·1274	−9·1102	+0·2376	24·13	+0·270	1·96713
13·2	+0·2084	−0·0505	+0·2589	13·24	+0·276	—
14·2	−0·3123	+0·0337	−0·3460	14·23	−0·359	—
34·2	+0·1618	−0·0651	+0·2269	34·12	+0·244	1·97333
23·1	+0·3553	+0·1219	+0·2334	23·14	+0·266	—
24·1	+0·3580	+0·1209	+0·2371	24·18	+0·270	—
34·1	+0·3404	+0·1272	+0·2132	34·12	+0·244	—

The first order coefficients, from Table II, are then regrouped according to the same primary subscripts as in Table I, and the work repeated precisely as before, as in Table III, but each coefficient of the second order is automatically calculated by this process in two ways and the work thus checked. Small errors introduced by the non-retention of insignificant figures may, of course, prevent complete agreement to the last place of decimals, and for this reason the coefficients of the first order were evaluated to four figures, although only three were required for the final result. In order to obtain the regression equation between changes in pauperism and changes in the three remaining variables, we require the three regressions $b_{12·34}$, $b_{13·24}$, and $b_{14·23}$ and, accordingly, must obtain the six standard deviations, $\sigma_{1·34}$, $\sigma_{2·34}$, $\sigma_{1·24}$, $\sigma_{3·24}$, $\sigma_{1·23}$, $\sigma_{4·23}$.

These are readily calculated and checked by means of the equations of the form—

$$\sigma_{1·34} = \sigma_1 (1 - r^2_{13})^{\frac{1}{2}} (1 - r^2_{14·3})^{\frac{1}{2}}$$
$$= \sigma_1 (1 - r^2_{14})^{\frac{1}{2}} (1 - r^2_{13·4})^{\frac{1}{2}}$$

given $\sigma_1 = 29·2$, $\sigma_2 = 41·7$, $\sigma_3 = 5·5$, $\sigma_4 = 23·8$; and the values found are:—

$$\sigma_{1·34} = 25·61, \qquad \sigma_{1·24} = 27·63, \qquad \sigma_{1·23} = 24·39,$$
$$\sigma_{2·34} = 36·06, \qquad \sigma_{3·24} = 4·73, \qquad \sigma_{4·23} = 22·86.$$

Hence, from the equations of the form

$$b_{12·34} = r_{12·34} \frac{\sigma_{1·34}}{\sigma_{2·34}},$$

we have

$$b_{12·34} = +0·325, \quad b_{13·24} = +1·383, \quad b_{14·23} = -0·383.$$

That is, the regression equation between changes in pauperism and changes in the other factors considered is

$$x_1 = 0{\cdot}325x_2 + 1{\cdot}383x_3 - 0{\cdot}383x_4.$$

To complete the work, we may calculate $\sigma_{1{\cdot}234}$, the standard error made in estimating x_1 from x_2, x_3, and x_4 by the above equation. The value is

$$\sigma_{1{\cdot}234} = \sigma_1(1-r^2_{12})^{\frac12}(1-r^2_{13{\cdot}2})^{\frac12}(1-r^2_{14{\cdot}23})^{\frac12}$$

$$= \sigma_1(1-r^2_{14})^{\frac12}(1-r^2_{13{\cdot}4})^{\frac12}(1-r^2_{12{\cdot}34})^{\frac12}$$

$$= 22{\cdot}8.$$

17. If, in accordance with the notation used for elementary cases in the paper already referred to, and that in a recent note by Mr. R. H. Hooker and myself,[*] we write

$$\sigma^2_{1{\cdot}23\ldots n} = \sigma^2_1(1-R^2_{1(23\ldots n)}), \qquad (15)$$

$R_{1(23\ldots n)}$ may be regarded as a coefficient of correlation between x_1 and the expression

$$e_{1{\cdot}23\ldots n} = b_{12{\cdot}34\ldots n}x_2 + b_{13{\cdot}24\ldots n}x_3 + \ldots + b_{1n{\cdot}23\ldots n-1}x_n. \qquad (16)$$

The value of R is accordingly a useful datum, as indicating how closely x_1 can be expressed in terms of a linear function of $x_2x_3 \ldots x_n$. It may be readily calculated either direct from the equation

$$1-R^2_{1(23\ldots n)} = (1-r^2_{12})(1-r^2_{13{\cdot}2})\ldots(1-r^2_{1n{\cdot}23\ldots n-1}), \qquad (17)$$

or from the value of $\sigma_{1{\cdot}23\ldots n}$ and σ_1, if previously obtained.

It is obvious from (17) that, since every bracket on the right is not greater than unity,

$$1-R^2_{1(23\ldots n)} \leqq 1-r^2_{12}.$$

Hence $R_{1(23\ldots n)}$ cannot be numerically less than r_{12}. For the same reason, rewriting (17) in every possible form, $R_{1(23\ldots n)}$ cannot be numerically less than r_{12}, r_{13}, ... r_{1n}, *i.e.*, any one of the possible constituent coefficients of order zero. Further, for similar reasons, $R_{1(23\ldots n)}$ cannot be numerically less than any possible constituent coefficient of any higher order. That is to say, $R_{1(23\ldots n)}$ is not less than the greatest of all the possible constituent coefficients of all orders, and is usually, though not always, markedly greater. Thus in the illustration of § 16, the value of $R_{1{\cdot}(234)}$ is $0{\cdot}626$, and the greatest correlation coefficient is $r_{12{\cdot}34} = 0{\cdot}458$. The sign of R is necessarily positive, for a positive increment in x_1 obviously corresponds on the average to a positive increment in $e_{1{\cdot}23\ldots n}$. More definitely, the standard deviation of $e_{1{\cdot}23\ldots n}$ is $\sigma_1 R_{1(23\ldots n)}$, and the regression of x_1 on $e_{1{\cdot}23\ldots n}$ is therefore $+1$.

Seeing that $\sigma^2_{1{\cdot}23\ldots n} = \sigma^2_1(1 - R^2_{1(23\ldots n)})$, and that $\sigma_{1{\cdot}23\ldots n}$ is a minimum, we may, alternatively, regard the values of the regressions as determined by the

[*] 'Roy. Stat. Soc. Journal,' vol. 59 (1906), p. 197.

condition that the correlation between x_1 and $e_{1\cdot 23\cdots n}$, viz., $R_{1(23\cdots n)}$, shall be a maximum.

18. It is obvious that equations (13) and (14) imply relations of an inverse kind, expressing coefficients of a lower order in terms of those of a higher order. Using the same method of expansion as in previous cases, we have

$$0 = \Sigma\, (x_{1\cdot 23\cdots n}x_{2\cdot 34\cdots n-1})$$

$$= \Sigma\, (x_1 x_{2\cdot 34\cdots n-1}) - b_{12\cdot 34\cdots n}\Sigma\, (x_2 x_{2\cdot 34\cdots n-1})$$

$$- b_{1n\cdot 23\cdots n-1}\Sigma\, (x_n x_{2\cdot 34\cdots n-1}).$$

That is

$$b_{12\cdot 34\cdots n-1} = b_{12\cdot 34\cdots n} + b_{1n\cdot 23\cdots n-1}b_{n2\cdot 34\cdots n-1}.$$

But by interchanging the suffixes, viz., 1 for n and n for 1,

$$b_{n2\cdot 34\cdots n-1} = b_{n2\cdot 13\cdots n-1} + b_{n1\cdot 23\cdots n-1}b_{12\cdot 34\cdots n-1}.$$

Substituting this value of $b_{n2\cdot 34\cdots n-1}$ in the first equation and simplifying,

$$b_{12\cdot 34\cdots n-1} = \frac{b_{12\cdot 34\cdots n} + b_{1n\cdot 23\cdots n-1}b_{n2\cdot 13\cdots n-1}}{1 - b_{1n\cdot 23\cdots n-1}b_{n1\cdot 23\cdots n-1}}. \tag{18}$$

This is the required equation for the regressions. The similar equation for the correlations is obtained at once by writing down the corresponding expression for $b_{21\cdot 34\cdots n-1}$ and taking the square root

$$r_{12\cdot 34\cdots n-1} = \frac{r_{12\cdot 34\cdots n} + r_{1n\cdot 23\cdots n-1}r_{2n\cdot 13\cdots n-1}}{(1 - r^2_{1n\cdot 23\cdots n-1})^{\frac{1}{2}}(1 - r^2_{2n\cdot 13\cdots n-1})^{\frac{1}{2}}}. \tag{19}$$

19. The general principle that any equation subsisting between such statistical constants as correlations, regressions, and standard deviations holds good for all secondary subscripts, applies also to the equation (3), which expresses the individual deviation of order p in terms of deviations of order zero. That is to say, we have, quite generally, k being any subscript or collection of subscripts,

$$x_{1\cdot 2\cdots kn} = x_{1\cdot k} - b_{12\cdot 3\cdots kn}x_{2\cdot k} - \ldots - b_{1n\cdot 2\cdots k(n-1)}x_{n\cdot k}. \tag{20}$$

For, if l be any one of the subscripts included under k, and if m denote the remaining subscripts, on expanding both sides of the equation in terms of deviations of order zero, the coefficients of $x_1, x_2, \ldots x_n$ are the same. The coefficients of x_l are equal if

$$b_{1l\cdot 2\cdots mn} = b_{1l\cdot m} - b_{2l\cdot m}\, .\, b_{12\cdot 3\cdots kn} - \ldots - b_{nl\cdot m}\, .\, b_{1n\cdot 2\cdots k(n-1)}.$$

But, replacing the regressions $b_{1l\cdot m}$, $b_{2l\cdot m}$, $\ldots b_{nl\cdot m}$ by product sums, this reduces to

$$\Sigma\, (x_{l\cdot m}\, .\, x_{1\cdot 2\cdots lmn}) = 0,$$

which is true by § 8, whether m denote a single subscript or an aggregate, or is absent, and equation (20) is accordingly correct. Remembering that

$$b_{12\cdot3\cdots k_n} = r_{12\cdot3\cdots k_n}\frac{\sigma_{1\cdot3\cdots k_n}}{\sigma_{2\cdot3\cdots k_n}} = r_{12\cdot3\cdots k_n}\frac{\sigma_{1\cdot23\cdots k_n}}{\sigma_{2\cdot13\cdots k_n}},$$

the equation may also be written in the useful form—

$$\frac{x_{1\cdot2\cdots k_n}}{\sigma_{1\cdot2\cdots k_n}} = \frac{x_{1\cdot k}}{\sigma_{1\cdot2\cdots k_n}} - r_{12\cdot3\cdots k_n}\frac{x_{2\cdot k}}{\sigma_{2\cdot13\cdots k_n}} - \ldots - r_{1n\cdot2\cdots k(n-1)}\frac{x_{n\cdot k}}{\sigma_{n\cdot12\cdots k(n-1)}}. \qquad (21)$$

20. In all the preceding sections no assumption of any kind has been made with respect to the form of the distribution of frequency, but the results may, of course, be applied to the special case of the normal distribution. Let $y_{12\cdots n}$ denote the value of the normal function for the combination of deviations $x_1, x_2, \ldots x_n$, and $y'_{12\cdots n}$ the value of the function when all deviations are zero, then we may write

$$y_{12\cdots n} = y'_{12\cdots n}.\exp{-\tfrac{1}{2}\phi}(x_1 x_2 \ldots x_n), \qquad (22)$$

the form of the function ϕ being determined by the fact that the distribution of every array must be normal, and that the mean of the array of any one variable associated with given types of the others must be the linear function of those types given by the general regression equation of the form (1). We must have, accordingly

$$\phi = \frac{x^2_1}{\sigma^2_{1\cdot23\cdots n}} + \frac{x^2_2}{\sigma^2_{2\cdot13\cdots n}} + \ldots + \frac{x^2_n}{\sigma^2_{n\cdot12\cdots(n-1)}}$$

$$- 2r_{12\cdot3\cdots n}\frac{x_1 x_2}{\sigma_{1\cdot23\cdots n}\sigma_{2\cdot13\cdots n}} - \ldots - 2r_{(n-1)n\cdot12\cdots(n-2)}\frac{x_{n-1}x_n}{\sigma_{(n-1)\cdot1\cdots(n-2)}\sigma_{n\cdot1\cdots(n-1)}}. \qquad (23)$$

But this expression may be thrown into several different forms. Thus, replacing the correlated variables, $x_1, x_2, \ldots x_n$, by the independent variables, $x_1, x_{2\cdot1}, x_{3\cdot12}, \ldots x_{n\cdot1\cdots(n-1)}$, we have the very useful form

$$\phi = \frac{x^2_1}{\sigma^2_1} + \frac{x^2_{2\cdot1}}{\sigma^2_{2\cdot1}} + \frac{x^2_{3\cdot12}}{\sigma^2_{3\cdot12}} + \ldots + \frac{x^2_{n\cdot1\cdots(n-1)}}{\sigma^2_{n\cdot1\cdots(n-1)}}. \qquad (24)$$

This expression may be shown to be identical with (23) by expanding in terms of deviations of order zero, and reducing the coefficients of the square terms by means of the equation

$$\frac{r^2_{n\cdot k}}{\sigma^2_{n\cdot k}} + \frac{1}{\sigma^2_n} = \frac{1}{\sigma^2_{n\cdot k}},$$

and those of the product terms by an equation derived at once from (19),

$$\frac{r_{13\cdot2k}r_{23\cdot1k}}{\sigma_{1\cdot2k}\sigma_{2\cdot3k}} - \frac{r_{12}}{\sigma_{1\cdot k}\sigma_{2\cdot k}} = -\frac{r_{12\cdot3k}}{\sigma_{1\cdot3k}\sigma_{2\cdot3k}}.$$

21. Several important results follow at once from the form of the expression (24) for the exponent ϕ. Since the variables are independent, the central value of the normal function, $y'_{12\cdots n}$, must be given by the product of the well-known expressions for the single variables, *i.e.*, we must have

$$y'_{12\cdots n} = N/(2\pi)^{n/2}\sigma_1\sigma_{2\cdot1}\sigma_{3\cdot12}\cdots\sigma_{n\cdot1\cdots(n-1)}. \tag{25}$$

22. Again, if we integrate the normal function in the form (24) with respect to x_1, treating the remaining variables, $x_{2\cdot1}$, $x_{3\cdot21}$, etc., as constants of integration, σ_1 is eliminated from y' and x_1 from ϕ, and all the remaining variables in the exponent contain the secondary suffix 1. If $x_{2\cdot1}$, $x_{3\cdot21}$, $\ldots x_{n\cdot1\cdots(n-1)}$ are then replaced by $x_{2\cdot1}$, $x_{3\cdot1}$, $\ldots x_{n\cdot1}$, ϕ may be written in the form (23) for these variables. Similarly, if we integrate again with respect to $x_{2\cdot1}$, $\sigma_{2\cdot1}$ is removed from y' and $x_{2\cdot1}$ from ϕ, and all the remaining variables in the exponent contain both secondary suffixes 1 and 2. If $x_{3\cdot21}$, $x_{4\cdot321}$, $\ldots x_{n\cdot321}$ are then replaced by $x_{3\cdot21}$, $x_{4\cdot21}$, $\ldots x_{n\cdot21}$, ϕ may be written in the form (23) for these variables. Clearly the process may be continued on the same lines. The correlation between all sets of deviations, of any one order, with the same secondary suffixes, is therefore normal correlation.

23. It follows that we may generalise at once the known formulæ for the probable errors of the constants of a normal distribution. Omitting the factor $0.674489\ldots$we have, standard error of a

Standard deviation σ_1 .... $\sigma_1/\sqrt{2N}$.
Correlation coefficient r_{12} .... $1-r^2_{12}/\sqrt{N}$.
Regression coefficient b_{12} .... $\sigma_{1\cdot2}/\sigma_2\sqrt{N}$.

The first is a well-known result; the last two are cited from the valuable memoir by Professor Karl Pearson and Mr. L. N. G. Filon.[*] But since $\sigma_{1\cdot k}$ is the standard deviation of the normally distributed variable $x_{1\cdot k}$, $r_{12\cdot k}$ the correlation between the normally distributed variables $x_{1\cdot k}$ and $x_{2\cdot k}$, and $b_{12\cdot k}$ the regression of $x_{1\cdot k}$ on $x_{2\cdot k}$, we must have, quite generally, k denoting as before either a single subscript or an aggregate, standard error of a

Standard deviation $\sigma_{1\cdot k}$ .... $\sigma_{1\cdot k}/\sqrt{2N}$.
Correlation coefficient $r_{12\cdot k}$ .... $1-r^2_{12\cdot k}/\sqrt{N}$.
Regression coefficient $b_{12\cdot k}$ .... $\sigma_{12\cdot k}/\sigma_{2\cdot k}\sqrt{N}$.   (26)

The last result may be readily verified against the formula arrived at by Professor Pearson and Mr. Filon, for the case of three variables, after pages of the most laborious work.[†] The first may be checked for the case of two

[*] 'Phil. Trans.,' A (1898), vol. 191, p. 229.
[†] *Loc. cit.*, equation xxxviii, p. 260.

variables, remembering the result of the same writers,* that the correlation between errors in σ_1 and in r_{12} is $r_{12}/\sqrt{2}$; for we have

$$\sigma_{1\cdot2} = \sigma_1 (1-r^2{}_{12})^{\frac{1}{2}};$$

$$\frac{d\sigma_{1\cdot2}}{\sigma_{1\cdot2}} = \frac{d\sigma_1}{\sigma_1} - \frac{r_{12}.dr_{12}}{1-r^2{}_{12}}.$$

Or, squaring both sides of the equation and summing, using $\epsilon_{1\cdot2}$ to denote the standard error of $\sigma_{1\cdot2}$,

$$\frac{\epsilon^2{}_{1\cdot2}}{\sigma^2{}_{1\cdot2}} = \frac{1}{2N} + \frac{r^2{}_{12}}{N} - \frac{2r_{12}}{1-r^2{}_{12}} \frac{r_{12}}{\sqrt{2}} \frac{1}{\sqrt{2N}} \frac{1-r^2{}_{12}}{\sqrt{N}} = \frac{1}{2N}.$$

23. The question of errors of sampling in the case of the coefficient of n-fold correlation, R, is not so simple, owing to the fact that the sign of the coefficient is essentially positive and, consequently, it is subject to biassed error. If, for instance, a series of variables are strictly independent, but values are found for r_{12}, $r_{13\cdot2}$, $r_{14\cdot32}$, etc., equal to δ_2, δ_3, δ_4,...then

$$1-R^2{}_{1(23\cdots n)} = (1-\delta^2{}_2)(1-\delta^2{}_3)...(1-\delta^2{}_n).$$

If the δ's are sufficiently small to enable us to neglect terms of the fourth order as compared with those of the second order, then we may write to the first approximation,

$$R^2{}_{1(23\cdots n)} = \delta^2{}_2 + \delta^2{}_3 + ... + \delta^2{}_n.$$

Or, summing for a number of samplings and substituting $1/N$ for $\Sigma(\delta^2)$ in each case, the root-mean-square value of R when the variables are strictly independent is

$$R_0 = (n-1)^{\frac{1}{2}}/N^{\frac{1}{2}}, \tag{27}$$

n being the number of variables and N the number of observations. R cannot be held with certainty to be of definite significance if not markedly greater than this, and if the number of observations be small compared with the number of variables, the critical value is rather unpleasantly large. Thus in the case of a recent investigation by Mr. R. H. Hooker into the relation between the weather and the crops, $n = 3$, $N = 21$, consequently $R_0 = \sqrt{\frac{2}{21}} = 0\cdot31$ (the value cited by him on my authority).† Clearly, if the number of observations be small, it is not worth while dealing with a large number of variables.

* *Loc. cit.*, equation xviii, p. 242.

† 'Roy. Stat. Soc. Journ.,' vol. 70 (1907), p. 7.

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The Gravitational Stability of the Earth.

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(Abstract.)

The problem of determining the conditions, as regards elasticity, in which a body of planetary dimensions can be gravitationally unstable, was attacked by J. H. Jeans.[*] To turn the difficulty arising from the fact that such a body is necessarily in a state of "initial stress," by which gravitation is balanced throughout its interior, he introduced an artificial external field of force to balance gravitation in the undisturbed body, and he thus dispensed with initial stress. A more direct method of treating the problem has been advocated by Lord Rayleigh.[†] In this method the stress at any point of the body, when disturbed from its equilibrium state, is taken to be compounded of two stress-systems; an initial stress of the nature of hydrostatic pressure, balancing gravitation in the undisturbed body, and an additional stress connected with the strain (reckoned from the initial state) by the same formulæ as connect stress with strain in a homogeneous isotropic elastic solid body which is slightly strained from an initial state of zero stress. In the first part of the present paper the equations of vibratory motion of the planetary body, assumed to be initially spherical, are formed in accordance with this method, and they are solved by means of spherical harmonics. The frequency equation is obtained, and the conditions that it may be satisfied by a zero value of the frequency are found. When these conditions are fulfilled the body is in a state of gravitational instability.

Let a denote the radius of the sphere, ρ_0 the density of the body in the initial state, μ its rigidity, $\lambda + \frac{2}{3}\mu$ its modulus of compression, γ the constant of gravitation. When the body is disturbed let (u, v, w) denote the displacement of any point (x, y, z), and Δ the dilatation, so that

$$\Delta = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z};$$

also let W denote the additional gravitation potential due to defect, or excess, of density, and to displacement of mass across the initial bounding surface. Then W satisfies the equation

$$\nabla^2 W = 4\pi\gamma\rho_0\Delta,$$

[*] London, 'Phil. Trans.,' Ser. A, vol. 201, 1903, p. 157.
[†] London, 'Roy. Soc. Proc.,' Ser. A, vol. 77, 1906, p. 486.

and, if the origin of co-ordinates is at the centre of the undisturbed sphere, the equations of vibratory motion are three equations of the type

$$\rho_0 \frac{\partial^2 u}{\partial t^2} = (\lambda + \mu)\frac{\partial \Delta}{dx} + \mu \nabla^2 u + \tfrac{4}{3}\pi \gamma \rho_0^2 x \Delta + \rho_0 \frac{\partial W}{\partial x}.$$

The quantities W, u, v, w must satisfy these equations, and they must also satisfy certain boundary conditions. One of these conditions is that the *displaced* bounding surface is the surface separating the region of space which contains the matter of the body from the external region. This condition is expressed as an equation which holds at the *initial* bounding surface, by regarding the potential W as due to a volume distribution of density within this surface and a superficial distribution upon it. The remaining boundary conditions express the vanishing of the surface tractions at the displaced bounding surface. These conditions also are replaced by equations which hold at the initial bounding surface, and these latter equations can be interpreted in the statement that the traction on the initial surface is a pressure, equal to the weight (per unit of area) of the material heaped up to form the radial inequality.

When the body is vibrating in a normal mode, the dilatation Δ at any point is proportional to the product of a certain function of the distance r of the point from the centre and a spherical surface harmonic of degree n. The displacement at any point is expressible in terms of this harmonic and its differential coefficients, by the aid of certain functions of r which are determined, and the radial component of displacement at any point is proportional to the product of a function of r and the same harmonic. The harmonic inequality of the initial bounding surface follows the same law , as the distribution of excess density at points of any spherical surface concentric with the boundary.

The condition that the frequency equation may be satisfied by a zero value of the frequency is an equation to determine the number $\tfrac{4}{3}\pi \gamma \rho_0^2 a^2 / (\lambda + 2\mu)$, which is denoted by $s^2 a^2$. The equation contains the number $\mu/(\lambda + 2\mu)$, which is denoted by ν; it also contains the integer n, which is the degree of the spherical harmonic specifying the mode of vibration. The homogeneous spherical planet is gravitationally unstable as regards displacements of the type specified by harmonics of degree n if the equation in question has a real positive root. It is proved that the equation has one, and only one, real positive root in each of the cases $n = 0$ and $n = 1$; it is proved further that it has no real root in either of the cases $n = 2$ or $n = 3$. The critical value of $(sa)^2$ in the case $n = 0$ (radial displacements) lies between 3 and 4 if $\nu = \tfrac{1}{4}$ and between 4 and 5 if ν is very small. The critical value in the case

$n = 1$ lies between 6·48 and 7·22 if $\nu = \frac{1}{4}$, and between 7·22 and 8 if ν is very small. The following table shows the corresponding values of the modulus of compression in dynes per square centimetre, in a body of the same size and mass as the earth :—

$s^2 a^2$.	Modulus of compression ($\nu = \frac{1}{4}$).	Modulus of compression (ν very small).
3	7·68 × 10¹¹	
4	5·76 × 10¹¹	
5	—	8·64 × 10¹¹
6·48	—	6·91 × 10¹¹
7·22	3·57 × 10¹¹	
8	3·19 × 10¹¹	4·79 × 10¹¹
	—	4·32 × 10¹¹

The modulus of compression of ordinary steel is about $1·43 \times 10^{12}$, that of glass $4·54 \times 10^{11}$, that of mercury $2·60 \times 10^{11}$.

The elastic constants of the earth, in its present state, can be estimated from the observed velocities of propagation of the three types of waves which are transmitted when a great earthquake takes place. There are two sets of " preliminary tremors " propagated directly through the earth with nearly constant velocities of about 10 kilometres per second and 5 kilometres per second, and a " main shock " propagated over the surface with a velocity of about 3 kilometres per second. The two sets of tremors have been identified with waves of dilatation and distortion, and the " main shock " with superficial waves of the type first investigated by Lord Rayleigh.* In the present paper reason is given for thinking that the manner of propagation is not much affected by gravitation and initial stress, and thus the observed values of the velocities of propagation of earthquake tremors and shocks would yield (i) for the seismic effective modulus of compression of the earth as a whole the value $3·69 \times 10^{12}$ dynes per square centimetre ; (ii) for the seismic effective rigidity of the earth as a whole the value $1·38 \times 10^{12}$ dynes per square centimetre ; (iii) for the seismic effective rigidity of surface rocks a value approximately equal to 6×10^{11} dynes per square centimetre ; (iv) for the seismic effective value of ν the number $\frac{1}{4}$. The corresponding value of $s^2 a^2$ is 0·625. As this is well below any critical value, it is concluded that the present state of the earth is far removed from one of gravitational instability.

In the second part of the paper an attempt is made to trace some of the consequences of the hypothesis that the elasticity of the earth was once

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* London, ' Proc. Math. Soc.,' vol. 17, 1885, p. 4, or ' Scientific Papers,' vol. 2, p. 441.

too small to secure stability in a homogeneous spherical configuration. J. H. Jeans, in the paper already cited, concluded that, if the earth at one time had so small a modulus of compression that a spherically symmetrical state of aggregation would have been unstable, it would have tended to take up a state in which there would have been excess of density in one hemisphere and defect in the antipodal hemisphere. To a first approximation the surface would have been spherical, but the centre of gravity would not have coincided with the centre of figure. Jeans found that, when a second approximation is made, the figure would have been slightly " pear-shaped," having a blunt end, a sharper end and a waist. In the same year, 1903, W. J. Sollas* published a paper in which, from an examination of the distribution of land and water, he also concluded that the figure of the earth resembles a " pear." The two pears have, however, little in common beyond the name; and Sollas' description of the figure points unmistakably to a mathematical description in terms of spherical harmonics of the third degree, while Jeans' theory is based entirely on the occurrence of harmonics of the first and second degrees.

If a homogeneous spherical planet were unstable at all, it would be unstable as regards radial displacements. It would, therefore, tend to pass into a state in which the density near the surface is less than the mean density. This is the actual condition of the earth, and it is at once accounted for by the hypothesis that the modulus of compression was once too small for a homogeneous state to be stable. The result, obtained in the first part of the paper, that the critical value of s^2a^2 in the case $n = 1$ is not very high in comparison with that which was found in the case $n = 0$, points to the conclusion that, if the mean modulus of compression of a planet, with a spherically symmetrical distribution of density, were sufficiently small, the planet, though stable for radial disturbances, might be unstable for disturbances specified by harmonics of the first degree. If the planet were at rest it would tend to take up such a form and state of aggregation as that described by Jeans. There would be excess of density in one hemisphere, and defect in the antipodal hemisphere, the excess or defect at any point being proportional, at any distance from the centre, to a spherical surface harmonic of the first degree, that is to say, to the distance of the point from the bounding plane of the hemispheres. The centre of gravity would be displaced relatively to the centre of figure towards that side where the density is in excess. The equipotential surfaces which lie outside the boundary of the figure and sufficiently near to it on the side where the density is in excess would cut it on the side where the density is in defect. If this were the case with the earth, the lithosphere (or nucleus) would cut the geoid (the equipotential

* 'Quart. J. Geol. Soc.,' vol. 59, 1903, p. 180.

surface with which the surface of the ocean coincides) so as to protrude from it towards one side. The land of the globe would consist of a single circular island which might occupy any fraction of the area of the surface. If a second approximation were made in the manner indicated by Jeans, a comparatively small island would be introduced at the antipodes of the central portion of the circular island indicated by the first approximation. If the earth were at rest, and the distribution of land and water were due to a past state of gravitational instability, the map would have the form just described.

It is necessary to consider the modification of these results on account of the rotation of the earth and the attraction of the moon. This attraction was, at one time, a nearly constant force, for the period of revolution of the moon was once nearly equal to the period of rotation of the earth. The figure of the earth would then have been more nearly an ellipsoid with three unequal axes than an oblate spheroid; and the inequalities of the attraction at different points of a spherical surface, having its centre at the centre of gravity, would have been expressible by means of a disturbing potential the terms of which would have been spherical surface harmonics of the second degree. In the present paper an examination is given of the effect of rotation upon a planet of which the modulus of compression is so small that, in the absence of rotation, a spherically symmetrical state of aggregation would be unstable. It appears that the type of disturbance would not be specified exclusively by harmonics of the first degree, but certain harmonics of the third degree would be introduced. When forces of the type of the attraction of the moon, involving a disturbing potential expressed by means of harmonics of the second degree, are taken into account, it is found that all the harmonics of the third degree would be introduced. Both the lithosphere and the geoid would be nearly spherical, more nearly oblate spheroids, still more nearly ellipsoids each with three unequal axes; and finally there would be a wrinkle on the ellipsoidal surface of the lithosphere expressible by means of harmonics of the third degree. There would also be excess of density on one side of a diametral plane and defect on the other side. The surface of the lithosphere, as determined by difference of level above or below the geoid, would be expressed by a sum of harmonics of the first, second, and third degrees.

If ever the earth as a whole had so small a modulus of compression that a spherically symmetrical state of aggregation would have been·unstable, the lithosphere would have consolidated in such a shape, and with such a situation relative to the geoid, as has been described; and we should expect to find traces of this shape and situation in the general features of the distribution of land and water, and still more in those features of the continental blocks and oceanic regions which are prominent at considerable depths below sea-level.

In the paper a spherical harmonic analysis, as far as harmonics of the third degree, is made of a distribution in which the value $+1$ is assigned to those points which are above sea-level, the value -1 to those points which are below mean-sphere-level, and the value 0 to intermediate points. The coefficients of the various harmonics are determined by a method of approximate integration, and the following spherical surface harmonic is thus found:—

$$(1161 \cos \phi + 824 \sin \phi) \sin \theta + 1407 \cos \theta$$

$$+(593 \cos \phi + 661 \sin \phi) \sin 2\theta + (-666 \cos 2\phi - 223 \sin 2\phi) \sin^2 \theta$$
$$+283 (3 \cos 2\theta + 1)$$
$$+(-144 \cos \phi + 9 \sin \phi)(\sin \theta + 5 \sin 3\theta)$$
$$+(-594 \cos 2\phi + 747 \sin 2\phi)(\cos \theta - \cos 3\theta)$$
$$+(82 \cos 3\phi + 325 \sin 3\phi)(3 \sin \theta - \sin 3\theta) - 347 (\cos 3\theta + \tfrac{3}{5} \cos \theta);$$

the quantities denoted by θ, ϕ are co-latitude measured from the North Pole and longitude east of Greenwich. A number of contour lines of the harmonic are drawn; and the results seem to show a sufficient agreement with the geographical facts to lend considerable support to the hypothesis which led to the conclusion that harmonics of the first, second, and third degrees should be predominant. From the fact that there are dynamical reasons why the lithosphere should have consolidated in a certain type of shape, and that its actual shape is approximately of this type, it appears probable that the shape has not changed greatly, but that many of the changes which have taken place have been of the nature of adjustments of the figure to changing dynamical conditions. This conclusion carries with it important consequences as to the general trend of events in geological history.

On the Dispersion of Artificial Double Refraction.

By L. N. G. Filon, M.A., D.Sc., Fellow and Lecturer in Mathematics of University College, London.

(Abstract.)

1. It is well known that glass compressed unequally in different directions behaves like a crystal whose optic axis is along the line of stress. If T_1, T_2 are the principal stresses in the wave front, μ_1, μ_2 the refractive indices of the two rays for which the directions of vibration are along T_1, T_2 respectively, then the relative retardation of the two oppositely polarised rays is

$$R = (\mu_1 - \mu_2)\,\tau = C\,(T_1 - T_2)\,\tau,$$

where τ is the thickness of glass traversed. C may be called the "stress-optical coefficient" of the glass. It differs for different glasses and in the same glass for different colours, but it is usually assumed independent of the value of the stress.

2. The experiments described in the paper were undertaken with a view to finding, for a number of glasses of different chemical composition, in particular borosilicates, how the coefficient C varied with the colour of the light used. No direct compression experiment could be employed, because it has been found impossible in such experiments to obtain a distribution of stress which remains uniform for all loads.

A new method was therefore devised which consisted in passing the light through two beams of glass placed at different levels and bent in a vertical plane by bending moments equal in magnitude and opposite in sense. It may be shown that if the coefficient C is, for monochromatic light, independent of the stress, such a combination is optically equivalent to a single slab under uniform compression or tension, according to the adjustment of level.

Light passed through such a combination between crossed Nicols is then analysed by a spectroscope. The spectrum is crossed by dark bands corresponding to wave-lengths for which R = integer multiple of λ. The measurement of λ then gives the required relative retardation.

The description of the method and the investigation of the various corrections fill the first half of the paper.

3. The second half is devoted to the experimental results and their

discussion. It is found that the observations are fairly fitted, on the average, by the formula

$$C = \frac{C_0}{1 - \lambda_0/\lambda},$$

where C_0, λ_0 are constants.

This formula cannot be justified theoretically and is to be regarded as an empirical formula, valid only within the limits of the visible spectrum, and then probably not for all glasses.

If, however, we try to fit some simple formulæ which are suggested by theoretical considerations, we find that they do not fit so well. The true formula is probably of the form

$$C = \Sigma \frac{C_p}{1 - (\lambda_p/\lambda)^2},$$

where $\lambda_p =$ wave-length, *in vacuo*, of light belonging to one of the free periods of the atoms of the glass.

Consideration of the constants in one case suggests that the free periods which are predominant in causing ordinary dispersion in the glass are different from those which are predominant in causing the dispersion of artificial double-refraction.

4. The method allowed the effects of tension and of pressure to be observed separately.

The constants C_0, λ_0 were found in each case to be sensibly different for tension and pressure. C_0 is usually greater for tension than for pressure, and λ_0 is invariably less. This difference, however, might also be accounted for by differences of adjustment which render the experiments for tension and pressure not strictly comparable. Until further data are available the effect must remain doubtful.

5. The results of careful observation have shown that in at least two glasses systematic deviations exist from the law

$$C = C_0/(1 - \lambda_0/\lambda).$$

These deviations are local in character, and their study leads to the conclusion that they are probably due to an absorption band corresponding to a free period efficient in producing double-refraction under stress. The results seem further to indicate that the effect of the stress is to change the number of the electrons which respond to vibrations in a plane through the line of stress relatively to the number of electrons responding to vibrations perpendicular to the line of stress, the actual periods of vibration being unaltered.

6. Analysis of the chemical composition of the glasses examined shows

that B_2O_3 increases and K_2O decreases the coefficient C_0. λ_0, on the other hand, does not seem to vary much for the range of chemical composition of the glasses in question. For such glasses, then, the dispersion of double-refraction appears roughly proportional to the stress-optical coefficient.

7. The experiments have also revealed that in one glass, for which the relation of stress to molar strain departed sensibly from linearity, the optical effect was proportional to the stress—that is to the molecular strain—and not to the molar strain; a result in accordance with what one might expect from the phenomena of double-refraction in viscous fluids in motion.

On the Refractive Indices of Gaseous Potassium, Zinc, Cadmium, Mercury, Arsenic, Selenium, and Tellurium.

By C. CUTHBERTSON and E. PARR METCALFE, B.Sc.

(Abstract.)

The present work forms a continuation of an enquiry begun by Mr. C. Cuthbertson[*] on the refractive indices of the vapours of elements not gaseous at ordinary temperatures.

The refractometer of Jamin was again employed, but tubes of fused silica were now used and other improvements introduced.

The following table exhibits the results obtained :—

Element.	Refractivities $(\mu-1)10^6$.					
	$\lambda = 6562.$	$\lambda = 5893.$	$\lambda = 5630.$	$\lambda = 5540.$	$\lambda = 5460.$	$\lambda = 5183.$
Potassium	negative	—	—	—	negative	
Zinc	1960	2050—2065	2020	—	2150 ?	2070
Cadmium	2675	2675	—	—	2725	2780
Mercury	1799*	1866	—	—	1882	1885
Arsenic	—	1552	—	—	1579	
Selenium	1520	1565	—	1560	1570	
Tellurium	2370	2495	—	—	2620	

* Subsequent work by Mr. Metcalfe renders it probable that the true value is $1\frac{1}{2}$ to 2 per cent. higher than this.—January 24, 1907.

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[*] 'Phil. Trans.,' A, vol. 204, p. 323, 1905.

Dispersion.

Except in the case of potassium, the dispersion is probably normal in direction in every case, and the apparent exceptions shown in the table are to be ascribed to errors of observation.

Refraction and Refraction Equivalents.

The gaseous refractivities of zinc, cadmium, and tellurium are higher than the highest (viz., that of iodine) of which we had previous knowledge.

The gaseous refractivities are compared with the refraction equivalents of Gladstone and others in the following table :—

	Refraction equivalents.						Refractivities now found (gaseous).			
	Gladstone.		Haagen.‡		Kannonikoff.§		$(\mu-1)10^6$.			
	Early.*	Later.†	R_μ.	R_A.	R_μ.	R_A.	λ 6562.	λ 5893.	λ 5460.	λ 5183.
As	15·4	15·4	20·22	18·84	—	—	—	1550	1580	—
Zn	10·2	9·8	19·89	18·64	9·8	9·4	1960	2060	2150	2070
Cd	13·6	13·1	—	—	13·03	12·66	2675	2675	2725	2780
Se	—	30·5	—	—	—	—	1530	1565	1570	—
H	1·3	—	—	—	—	—	—	139	—	—

* 'Journal Chem. Soc.,' 1870, p. 101; 'Phil. Trans.,' 1870, p. 9.
† 'American Journal of Science,' 3, vol. 29, 1885, p. 57.
‡ 'Pogg. Ann.,' vol. 131, 1867, p. 127.
§ 'Journal für Praktische Chemie,' vol. 31, 1885, p. 339.

The results are very curious. Gladstone's refraction equivalent for arsenic is about 12 times that for hydrogen, while the gaseous refractivity is 11 times that of hydrogen. But the values of Gladstone for zinc and cadmium are just half those now obtained. Haagen, however, has a value for zinc which corresponds fairly well with the refractivity. Finally, Gladstone's value of selenium is about double that shown by the refractivity.

Relative Refractivities of the Elements.

The values now obtained confirm previous observations of the periodicity of this function and its connection with the atomic weight. They also strengthen the belief in an intimate connection with the valency.

On the Absorption of Water by Cotton and Wool.

By Morris W. Travers, D.Sc., F.R.S., Director of the Indian Institute of Science, Bangalore.

In a footnote to my paper entitled " The Law of Distribution where one of the Phases possesses Mechanical Rigidity,"[*] I attempted to show how the results obtained by Professor Trouton[†] for the absorption of water vapour by cotton could be reconciled with those obtained by me in the case of similar systems, such as carbon dioxide and amorphous carbon. As the apparatus I had employed in the investigation referred to was particularly suited to the accurate measurement of low pressures, I obtained Professor Trouton's permission to repeat his work, and to investigate the relationship of pressure and concentration for the systems water-cotton and water-wool at the temperature of melting ice.

I was particularly anxious to redetermine the lower portions of the curves, for as in Professor Trouton's experiments the material was dried at the air temperature, it appeared probable that it contained water at the commencement of the experiment, and that the true origin of his curves lay further to the left than the results appeared to show. If this were the case, the true curve representing equilibrium in the system water-cotton might closely resemble those representing equilibrium in the system carbon dioxide and amorphous carbon.

The measurements were made by means of the apparatus described in the previous paper.[‡] About 10 grammes of cotton or wool was contained in the bulb a, which formerly contained the amorphous carbon, and to the bottom of the bulb was sealed a tube connected with an arrangement such as was described by Professor Trouton, for admitting successive quantities of water. The apparatus was connected through a large tube containing pentoxide of phosphorus with a Töpler pump and, after exhaustion, the bulb containing the wool or cotton was maintained at the temperature of boiling water for four hours, so as to remove all traces of moisture from the material. The methods of manipulation and of making the observations have already been described.

The results are shown on the accompanying curves. It appears that in

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[*] 'Roy. Soc. Proc.,' A, vol. 78, p. 9.

[†] 'Roy. Soc. Proc.,' A, vol. 77, p. 292.

[‡] Loc. cit., p. 11.

neither case do the curves exhibit any tendency to bend to the right, as do those representing the results of Professor Trouton's experiments. Experimental difficulties prevented me from extending them further.
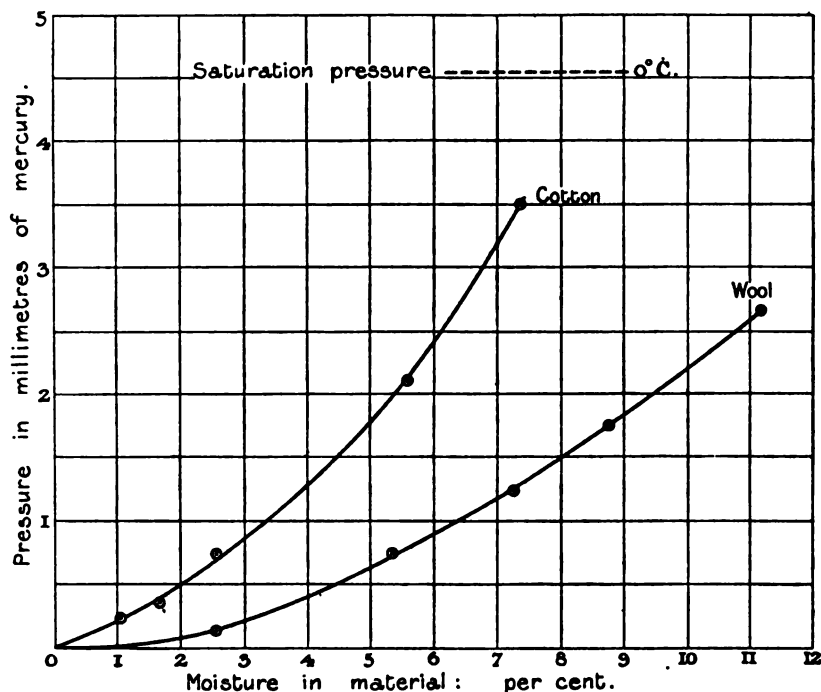
I have already expressed the opinion that the absorption of vapours by amorphous substances involves the formation of solid solutions, though, since amorphous substances are not physically distinct from liquids, the term "rigid" solution would be more exact. Crystalline solids would only absorb, in the strict sense, the vapours of substances which, in the solid phase, were isomorphous with them; and if they exhibited absorptive power towards other substances it might be set down to surface condensation or to chemical action.

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The Total Ionisation of Various Gases by the α-Rays of Uranium.*

By T. H. LABY, 1851 Exhibition Research Scholar of the University of
Sydney; Emmanuel College, Cambridge.

The first experiments on the total relative ionisation produced by the Becquerel rays from uranium oxide were made by Prof. Rutherford.[†] With a brass ball of 1·1-cm. radius coated with uranium oxide placed inside a metal coated bell-jar of 6·5-cm. radius for containing the gases, the ball being connected to an electrometer and the bell-jar raised to a potential of 800 volts, he found the following values for the total ionisation:—

Air $\equiv$ 100, hydrogen 95, oxygen 106, carbonic acid 96, coal gas 111, hydrochloric acid gas 102, ammonia 101.

An investigation of the conductivity of gases under the action of Becquerel rays was next made by the Hon. R. J. Strutt,[‡] using, among other agents, the easily-absorbable α-rays from barium radium carbonate, polonium, and a uranium preparation. He obtained for the relative conductivities the following values, which are proportional to the densities of the gases, except in the case of hydrogen:—

Gas.	Relative density.	Relative conductivity.			
		Radium rays, absorbable type.	Polonium rays.		Uranium rays.
			I.	II.	
Hydrogen..............	0·069	0·218	0·226	0·219	0·213
Air	1·00	1·00	1·00	1·00	1·00
Oxygen	1·11	—	1·16	—	—
Carbon dioxide	1·53	—	1·54	—	—
Cyanogen............ ...	1·86	—	1·94	—	—
Sulphur dioxide	2·19	1·92	2·04	2·03	2·06
Chloroform	4·32	—	4·44	—	—
Methyl iodide	5·05	3·74	3·51	3·47	3·55
Carbon tetrachloride	5·31	—	5·34	—	—

* The results of this investigation have been briefly stated by Prof. J. J. Thomson in his 'Conduction of Electricity through Gases,' 2nd edition, p. 369, October, 1906.

† 'Phil. Mag.,' vol. 47, p. 136, January, 1899.

‡ 'Phil. Trans.,' A, vol. 186, p. 507 (1901).

Experimental Methods.

Uranium oxide, U_3O_8, was selected as a source of α-rays for several reasons. Madame Curie has shown it to be of very constant activity; $0.9947(=1-0.0074 \times \frac{4}{5.7})$ of the ionisation in a slab of 4 cm. of air over a film of 0.0012 gramme per square centimetre is produced by the α-particles*; the range of its α-particle was believed to be short, which meant smaller total voltages would be required to obtain a saturation current; and finally uranium has no emanation, the cause of experimental difficulties with radium.

Apparatus.—The ionisation vessels were two similar cylindrical brass vessels, one of which is drawn to scale in fig. 1.
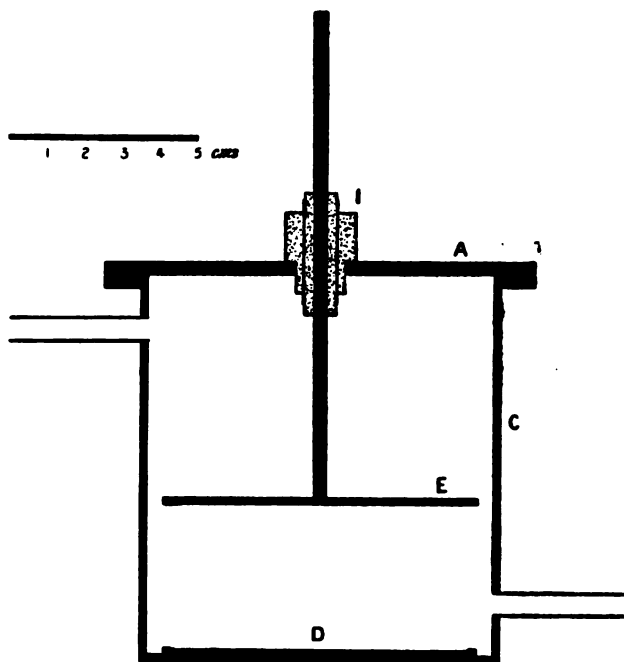
FIG. 1.

The brass top A was fastened by means of screws, an indiarubber washer made a gas-tight joint. The disc electrode E, attached to a rod passing through the guard ring insulator I of vulcanite, could be placed at a desired distance from the disc D which was coated with 0.0067 gramme per square centimetre of the dark-green oxide, U_3O_8. The joints in I were made gas-tight with shellac.

* Rutherford and Grier, 'Phil. Mag.,' p. 315, September, 1902.

In order that the results obtained should be, as far as possible, independent of the electrometer, a null method for measuring the total ionisation was at first tried. The electrode E of the standard air vessel C, and the similar electrode E′ of a vessel C′ containing the gas under examination were connected to the Dolezalek electrometer. One vessel was connected to +400 volts, the other to −400 volts, and the excess (or defect) of the current from C′ over that from the standard C was measured. But a passable concordance in successive observations (with the conditions unchanged) was not obtainable either when the rate of deflection of the electrometer was observed or when the electrometer was allowed to charge up for a definite time, or when a Wilson tilted electroscope was substituted for the electrometer. The cause of this want of concordance in the observations could not be found, and appeared not to be due to imperfect shielding, or the keys, etc. The electroscope was quite free from irregularities when directly tested. The null method was consequently abandoned, and the apparatus was arranged as shown in fig. 2.
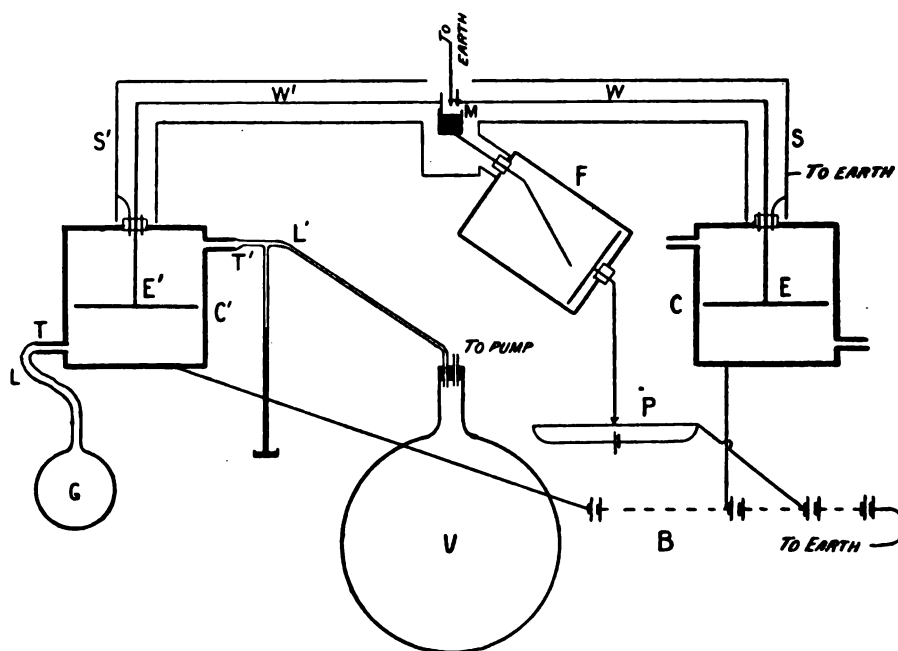
FIG. 2.

The ionisation vessels (already described) were used and could be alternately connected to the Wilson electroscope F. The vapour or gas, generated in G, entered the vessel C′ through T and passed out through T′,

which was connected with a large glass vessel V, to a mercury-pressure gauge, and to a pump. For adjusting the pressure in C' there were clips at L' and L. B represents a set of 500 (in some experiments 900) small lead accumulators with the positive terminal earthed. The wires W, W' for connecting the electrodes E and E' to the mercury cup M attached to the gold leaf of the electroscope F were made as short as possible, and passed through brass tubes S, S' connected to earth.

Method of using Electroscope.—With the leaf of the electroscope to earth, a small adjustment, if necessary, of the potential of the charged plate was made by means of the potential wire P till the leaf was exactly at the zero of the reading microscope scale. To determine the amount of ionisation in either of the vessels, the electrode E of the vessel was connected to the gold leaf through the mercury cup M, and the time taken between when the connection to earth of the mercury cup was broken and when the leaf (rapidly) passed the last division of the scale. The constancy of the sensitiveness of the electroscope was checked by means of the standard vessel, which, being undisturbed, gave a constant current. The following readings, obtained with the standard vessel, show the agreement of successive observations—

1.5.06...... 50 scale divs. 36·3, 35·8, 36·4, 36·5 secs. Mean, 36·2 secs.

2.5.06...... „ „ 36·3, 36·6, 36·1 secs. Mean, 36·3 secs.

11.5.06...... 33·6, 33·6, 33·6, 33·6 secs.

14.5.06...... 33·7, 33·5 secs.

With air in the vessel C', E' was connected to the electroscope and the ionisation measured. Then, when a gas was under examination, it was passed for an hour or more through C' to completely displace the air from it; when a vapour was under examination, the vessel C' was exhausted to a pressure of a few centimetres of mercury, and the vapour from the volatile liquid was boiled through. The pressure in the vessel was kept constant by means of the clips at L' and L and the large exhausted glass globe. With the electrode, the U_3O_8, and the voltage undisturbed, the ionisation in the gas or vapour was determined. The gas was swept out by air and the ionisation again measured. The ratio of the ionisation of the gas to the mean of the two air values gave the relative ionisation.

Range of the α-Particle from Uranium.

This range, which had not been estimated when the experiments were begun, determines the least distance allowable between the plates E' and D',

if there is to be complete absorption of the α-rays in the intervening gas. Since a high E.M.F. is necessary in order to obtain a saturation current, it is desirable to have this distance as small as complete absorption will allow. The thickness of the air ionised by the uranium oxide disc was actually found by slightly indirect method. With the plates at a fixed distance apart, the ionisation with air between them was observed at several pressures. Since
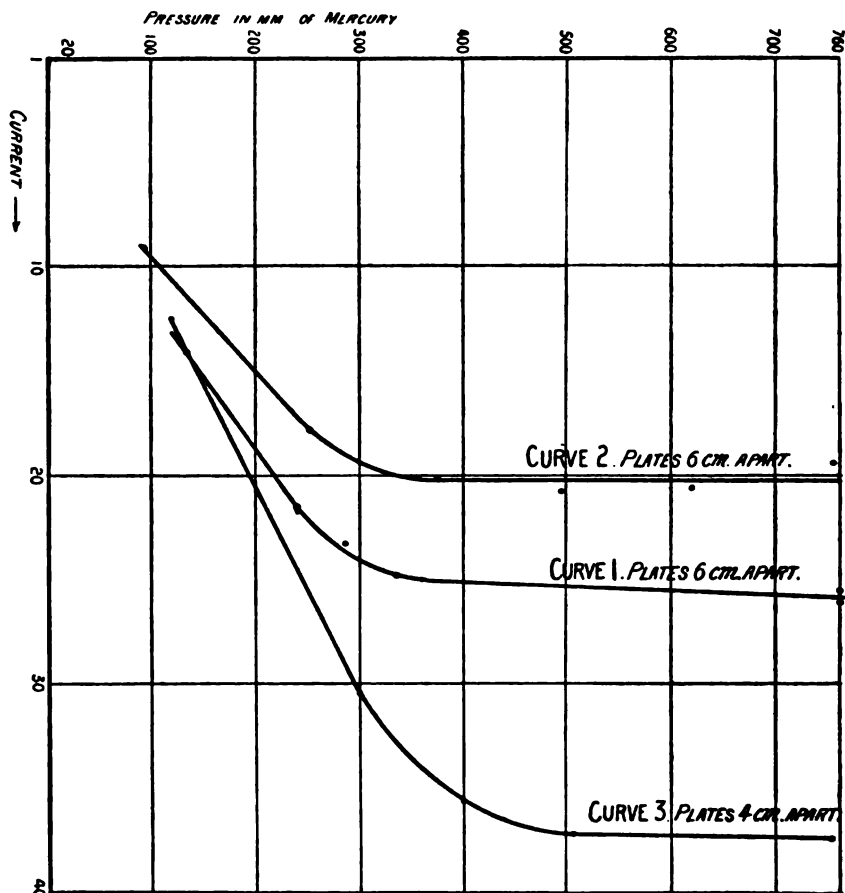
Pressure-current curves for air.

the stopping power of a gas varies as the pressure, this was equivalent to observing the ionisation at several distances between the plates, but has the distinct advantage that the electrical capacity of the apparatus is not sensibly different in different experiments. The results of two experiments with the electrode E at 6 cm. from the uranium and one with it at 4 cm. are plotted in curves 1, 2, and 3; in each case the vessel was at −1000 volts. The unit of current is different for each curve. The approximate pressures at which

the ionisation begins to decrease and (assuming the proportionality of stopping power and pressure) the equivalent distances in air at 760 mm. are as follows:—

Distance between plates.	Curve.	Decrease of ionisation at—	Equivalent distance.
cm.		mm.	cm.
6	1	380	3·0
6	2	360	2·8
4	3	290	2·63

From these curves it was concluded that a slab of air at 760 mm., 4 cm. thick, was more than sufficient to completely absorb all the α-rays from uranium. With other gases, the distance between the plates, and the pressure were so adjusted as to give a stopping power equivalent to 4 cm. of air. That this is sufficient is confirmed by Prof. Bragg,* who has recently found that the range of the α-particle of uranium is very nearly equal to that of the α-particle of radium, i.e., 3·5 cm.† While these curves show the minimum distance allowable between the plates, a consideration of the distribution of the ionisation above the layer of uranium oxide used shows that the range could not be found with any accuracy from them.

Saturation Voltage.

As it is necessary in determining the total ionisation to use a saturation current, the voltage per centimetre giving this had to be known. For air, nitrous oxide, and sulphur dioxide, the current-voltage per centimetre curves are given in curves 4 and 5, and portions of similar curves for NH_3, $(C_2H_5)_2O$, C_5H_{12}, C_2H_5Cl and CH_3CHO. The dotted portion of the curve for air between 215 and 260 volts per centimetre was obtained in a separate experiment to the rest of the curve. While 130 volts per centimetre give a saturation current in air, the curve for sulphur dioxide shows that this gas is not saturated with 600 volts per centimetre.

The tables on p. 212 state the values from which the curves have been drawn.

Source of Gases.

The nitrous oxide used was obtained from a partially emptied cylinder of the compressed gas.

The ammonia (from a cylinder) was dried by being passed over solid potassium hydroxide.

* 'Trans. Roy. Soc. South Australia,' vol. 29, p. 16, April, 1906.
† Bragg and Kleeman, 'Phil. Mag.,' p. 318, 1905, 2.

Volts per centimetre.	Current.	Volts per centimetre.	Current.

Air at atmospheric pressure.

13	18·5	98	28·6
27	22·4	116	29·6
42	24·4	123	28·6
69	27·0	139	29·8
125	23·75	138	23·81
215	27·3	260	27·3

Voltage used in total ionisation experiments was 130—600 volts per centimetre.

Nitrous oxide at atmospheric pressure.

7	5·6	143	23·2
13	13·0		
34·5	17·4	103	20·0
50	18·4	126	20·5
73	20·1	143	20·7
98	22·0		

Voltage used in experiments on total ionisation was 140 volts per centimetre.

Sulphur dioxide at 765 mm. pressure.

46	20·8	466	33·1
125	25·5	533	34·0
266	29·6	600	34·7

Voltage used in experiments on total ionisation was 600 volts per centimetre with SO_2 at 500 mm. press.

Pentane at 220 mm. pressure.

200	48·6	250	48·8

Voltage used = 200—250 volts per centimetre.

Ammonia at atmospheric pressure.

100	43·5	200	48·1
150	47·9		

Voltage used = 320—360 volts per centimetre.

Ethyl ether at 210 mm. pressure.

260	34·4	330	34·3

Voltage used = 250 volts per centimetre.

Aldehyde at 380 mm. pressure.

200	34·9	250	34·8

Voltage used = 200 volts per centimetre.

Ethyl chloride at 270 mm. pressure.

280	51·8	360	52·9
820	52·4		

Voltage used, 360 at 208 mm., equiv. to 540 at 300 mm.

CURVE 4

CURVE 5.
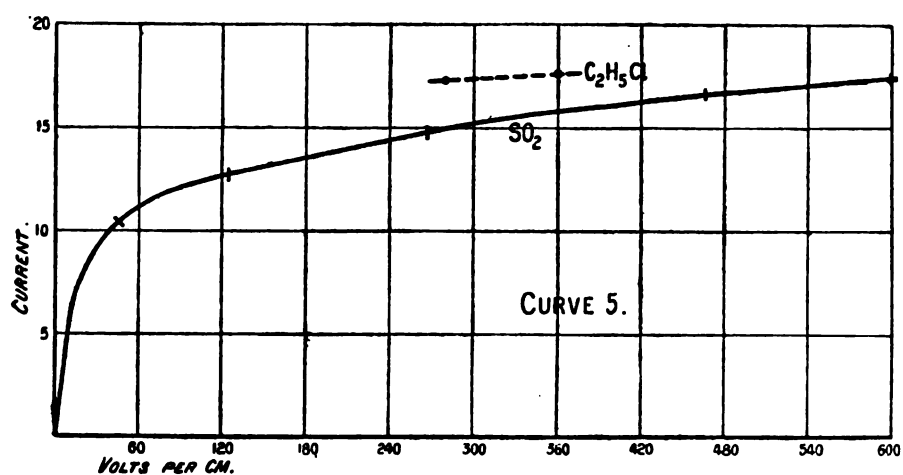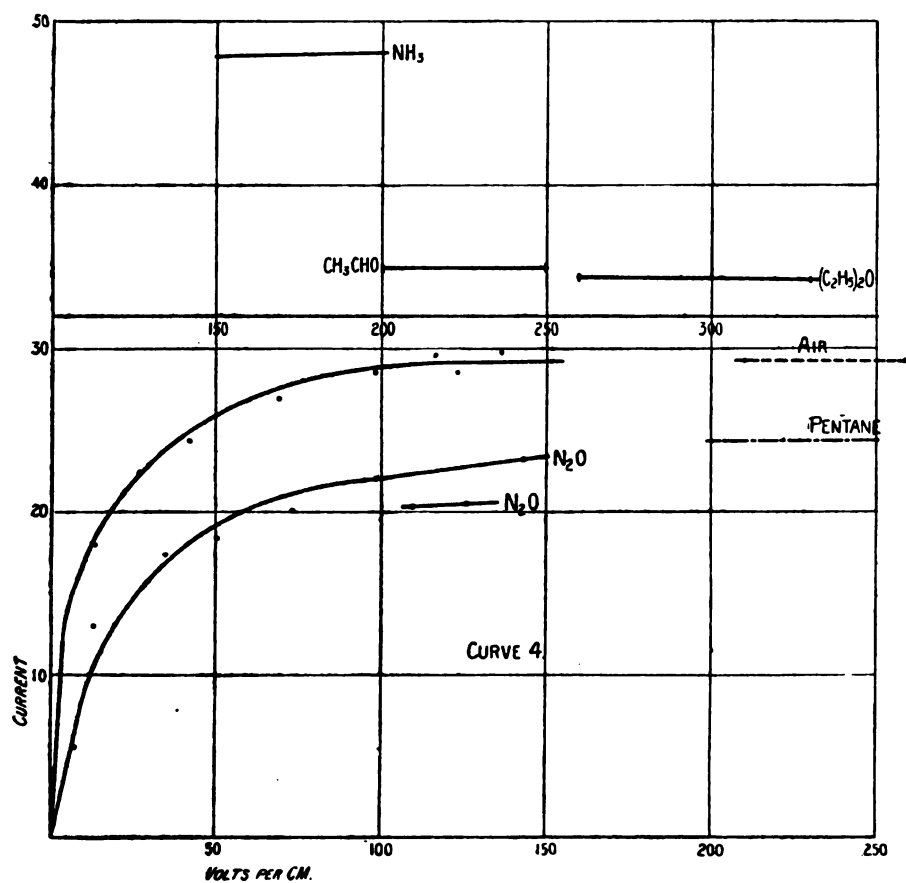
The carbon dioxide was from a cylinder.

Sulphur dioxide from the liquefied gas in a glass syphon was passed through a long drying tube of sulphuric acid into the ionisation chamber which had been previously filled with dry air, in order to avoid fumes of sulphurous acid.

The acetylene obtained from calcium carbide and water was dried with sulphuric acid.

The methyl bromide, ethyl chloride, ethyl ether, pentane, and aldehyde were the preparations of Kahlbaum, and were fractionally distilled through the ionisation vessel, which had been exhausted to a low pressure (about 10 cm.) before the vapours were admitted. In this way the liquids were purified and the air intially present in the ionisation vessel removed. The presence of 4 per cent. of air as impurity in pentane vapour would be necessary to affect the amount of ionisation to 1 per cent.

The ionisation of each gas, as already mentioned, was found by determining the total ionisation, first with air in the vessel, then with the gas in it, then in nearly all cases with air again. Thus direct comparisons with air were made.

Experimental Results.

Details are given in the following table for each gas examined, of its pressure, the distance between the uranium oxide and the electrode above it, the effective stopping power of the intervening gas at that pressure compared with a slab of air 1 cm. thick at 760 mm. and, finally, the relative total ionisation compared with air $\equiv$ 1.

Gas.	Pressure.	Distance between plates.	Effective stopping power.	Volts per centimetre.	Total ionisation.
		cm.			
Air	760	4	4·0	—	1·00
Nitrous oxide............	755	6	8·7	140	0·99
Ammonia	760	5	4·4	360	0·90
Carbon dioxide	760	3	4·5	130	1·03
Acetylene	763	3·5	3·8	228	1·27
Pentane	200—290	4	3·8—5·5	200—250	1·345
Acetaldehyde.............	283	5	3·5	200	1·05
Ethyl ether	200—210	4—3	3·6—2·8	250—330	1·29
Methyl bromide	371	4	4·08	250	1·02
Ethyl chloride	250	5	3·88	360	1·18
(Sulphur dioxide*	500	3	3·7	600	0·94)

* The voltage for sulphur dioxide, 600 volts per centimetre, did not give a saturation current. Mr. Kleeman has examined this gas by Prof. Bragg's method (see later), and found with 1500 volts per centimetre, $R.I = \frac{1}{1·70} \times 2·01 = 1·18$.

It is necessary to consider the magnitude of two possible corrections to the above results: the one is the correction arising from the fact that some of the α-particles from the edge of the uranium disc strike the walls of the vessel and their ionising power is only partly spent in the gas, the other is the ionisation due to β- and γ-rays from the uranium.

When the pressure of a gas in the ionisation vessel was such that its effective stopping power was the same as that of the air with which it was compared, then it can be said from the investigations of Prof. Bragg and Mr. Kleeman that the range and velocity of all the α-particles, including the ones which strike the sides of the vessel, were unchanged when the gas in the vessel was replaced by air and the ionisations found could be strictly compared. The effective stopping powers, however, of the gases were not in all cases the same as that of air at atmospheric pressure, as is shown below.

Effective Stopping Powers.

Gas.	Pressure used in millimetres, *p.*	Stopping power, at 760 mm.; air ≡ 1.	Effective stopping power, at pressure *p.*
Nitrous oxide............	755	1·46*	1·46
Ammonia	760	0·89 cal.	0·89
Carbon dioxide	760	1·47	1·47
Acetylene	763	1·11	1·11
Pentane	200—290	3·59	0·94—1·37
Acetaldehyde	283	1·88†	0·7
Ethyl ether...............	200—210	3·40	0·9—0·94
Methyl bromide.........	371	2·09	1·02
Ethyl chloride	250	2·36	0·78
Sulphur dioxide.........	500	1·70†	1·12

* 'Phil. Mag.,' May, 1906.
† Unpublished determination by Mr. Kleeman.

With nitrous oxide (stopping power 1·46) at atmospheric pressure in the ionisation vessel, some of the α-particles from the edge of the uranium disc with paths directed towards the sides would spend more of their ionising energy in this gas than they would spend when the vessel contained air. The proportion of these α-particles to the whole number must be small from the evidence of the experiments given on p. 216, in which the pressure of the gas was varied within certain limits, and thus also the effective stopping power, and yet no certain change in the ionisation was observed.

From these experiments it is seen that the correction under consideration is so small that it only certainly appears in the case where the stopping power was doubled (the second of the air results on p. 216). In the total ionisation experiments, only in the case of N_2O and CO_2 was the effective

Gas.	Pressure in millimetres of Hg.	Effective stopping power.	Ionisation.
Air ....{	752 505	0·99 0·66	37·5 37·2
Air ....{	760 380	1·0 0·5	25·9 25·0
Pentane ....{	220 270	1·04 1·27	48·8 48·8
Pentane ....{	250 280	1·18 1·32	48·6 48·6
Methyl bromide...{	372 410	1·02 1·13	44·6 44·8

stopping power of the gas different by as much as 40 per cent. from the air with which the ionisation of these gases was compared. For such a difference of stopping power the correction would be, from the analogy of the first air results above, not more than 0·7 per cent., or of the same magnitude as the experimental error of a determination of ionisation. In the case of the other gases the correction was smaller.

The ratio of the ionisation in a layer of air 4 cm. thick due to the β-rays to the ionisation due to the α-rays from the U_3O_8 disc used may be found thus. The intensity I of the β-rays from a layer of uranium oxide, of thickness d, is given by the relation

$$I = I_0(1 - e^{-\lambda d}),$$

where I_0 is the intensity of the β-rays from a very thick layer, and λ divided by the density of the uranium oxide is 6·3. This gives for the layer of uranium oxide of 0·0067 gramme per square centimetre used in the experiments of this paper

$$I = 0·041 \, I_0.$$

Now Rutherford and Grier[*] determined the relative amount of ionisation produced in a slab of air 5·7 cm. thick by the β- and α-rays from a layer of uranium of 0·0012 gramme per square centimetre, and found the ionisation due to the β to be 0·0074 of that due to the α-rays.

For this layer

$$I = 0·0079 \, I_0.$$

Thus the β-rays from the thicker layer have 5·2 times the intensity of those from the thinner layer. By plotting the values found by Rutherford and McClung[†] for the saturation current from a varying thickness of uranium oxide, it is found that the ionisation due to the α-rays of the

* 'Phil. Mag.,' p. 315, September, 1902.
† 'Phil. Trans.,' A, vol. 196, p. 25, 1901.

thicker of the above layers is 3·1 times that due to the thinner. Thus

$$\frac{5·2 \times 0·0074}{3·1} = 0·0124$$ of the ionisation produced by the thicker layer

(0·0067 gm./cm.²) is due to β-rays.

And since the relative ionisations produced by β-rays in different gases are very similar to those of the α-rays, this 1·2 per cent. of β-ionisation gives rise to a negligibly small correction.

The γ-rays produce less ionisation than the β, so need not be considered.

Comparison of Ionisations due to α-Uranium and Radium Rays.

Since this research was concluded, Prof. Bragg has published* the results of his work "On the Ionisation of Various Gases by the α-Particles of Radium."

He found the total relative ionisation by a method essentially different to the one used by the writer. It is based on the following considerations. When the ionisations in air, produced in a shallow (3 mm. deep) horizontal chamber by the approximately vertical rays obtained when a grid of narrow vertical tubes is placed over radium bromide, are plotted against distances from the radium film, a curve of this kind is obtained.

Prof. Bragg shows that changing the pressure, temperature, or gas alters the curve so that " the ordinates are multiplied by some factor, and all the abscissæ divided by the same factor," so that the product R × I of the coordinates of a point such as P (where the top portion of the RaA curve meets the side of the RaC curve—a point readily found) is proportional to the area of ABPCD, i.e., to the total ionisation produced by the RaC. Prof. Bragg has found the value of R.I for a number of gases. This

Fig. 3.

method seems to be more complicated, and to be based on more assumptions
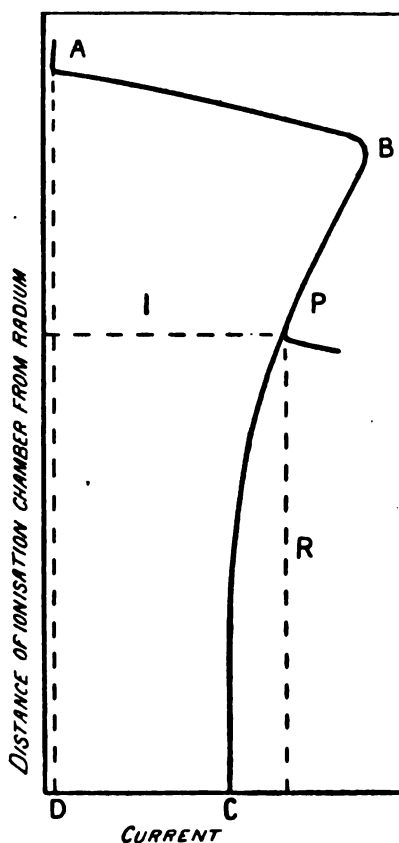
* 'Trans. Roy. Soc. South Australia,' vol. 30, October, 1906.

than the one used by the writer; but it has the great advantage for gases requiring a large saturation voltage (such as sulphur dioxide and ethyl chloride) that this voltage can be more readily obtained by using it.

The following is a comparison of the total ionisation due to α-particles found for the gases done in common by Prof. Rutherford, Prof. Bragg, and myself:—

Total Ionisation due to α-rays.

Gas.	Rutherford. Uranium.	Author. Uranium.	Bragg. Radium C.
Air	1·00	1·00	1·00
Nitrous oxide	—	0·99	1·05
Ammonia	1·01	0·90	—
Carbon dioxide	0·96	1·03	1·08
Acetylene	—	1·27	1·26
Pentane	—	1·345	1·35
Ethyl ether	—	1·29	1·31
Ethyl chloride............	—	1·18	1·30

The writer's values for CO_2 and N_2O may be less than the true values, for these were the first gases tested, and not quite sufficient voltage was available to obtain a fully saturated current.

It is evident from the table that the relative total ionisation is independent of the range and initial velocity of the α-particles producing it, for the RaC α-particle has probably double the range of the uranium one. The agreement of the results of two such different methods of measurement as those of Prof. Bragg and the writer is of interest.

The Density Rule.

When the details of the Hon. R. J. Strutt's experiments are considered, it appears that his conductivity of a gas divided by its stopping power gives approximately the total ionisation for that gas. As he found the conductivity of a gas was proportional to the density, we have

$$I_t = \rho/s,$$

where I_t is the total relative ionisation, ρ the density, and s the stopping power of the gas. On comparing the total ionisation calculated in this way with the ionisation found in the writer's experiments, there is seen to be little agreement.

Since the total ionisation I_t is the ionisation in a slab of given area of the gas under consideration of thickness equal to the range R of the α-particle in that gas, then the ionisation per unit volume I is $I_t . 1/R$, or $I_t . s$, where s is the stopping power, the reciprocal of the range R. Further, on account of the similarity of shape of the ionisation-distance curves for different gases, which has been shown to exist by Bragg, the ionisations per unit volume I

Gas.	Density ρ.	Formula.	Stopping power.		Total ionisation.	
			Experimental s.	Calculated by square root rule.	Found I_t.	Calculated by Strutt's rule, $I_t = \rho/s$.
Air (standard) ...	1·00	—	1·00	1·00	1·00	1·00
Nitrous oxide	1·52	N_2O	1·46	1·52	0·99	1·04
Ammonia	0·59	NH_3	—	0·89	0·90	0·66
Carbon dioxide ...	1·53	CO_2	1·47	1·51	1·03	1·05
Acetylene {	0·97 / 0·905 cal.	C_2H_2	1·11	1·17	1·27	0·87
Pentane	2·50	C_5H_{12}	3·59	3·86	1·345	0·71
Acetaldehyde	1·53 cal.	$CH_3.CHO$	1·88	1·96	1·05	0·82
Ethyl ether	2·67	$(C_2H_5)_2O$	3·40	3·67	1·29	0·78
Methyl bromide...	3·31 cal.	$CH_3.Br$	2·09	2·03	1·02	1·58
Ethyl chloride ...	2·22	$C_2H_5.Cl$	2·36	2·31	1·18	0·94

obtained in this way are comparable, for they are the ionisations for equal velocities of the α-particle. On account of the equality of the number of molecules in unit volume of different gases under similar conditions, this I is also the "specific molecular ionisation," as Bragg has pointed out. Kleeman has suggested it is an additive atomic property, and Bragg that it is approximately proportional to the volume of the molecule ionised. The agreement of these views with the writer's results will be seen from the following table :—

Gas.	Total ionisation I_t.	Stopping power s = 1/R.	Specific molecular ionisation, or ionisation per cubic centimetre, $I_t.s = I$.	Calculated specific molecular ionisation by additive rule of Kleeman.	Molecular volume.	Molecular volume. / Specific molecular ionisation
Air	1·0	1·0	1·0	1·00*		
N_2O	0·99	1·46	1·45	1·45*		
NH_3	0·90	0·89 cal.	0·80	1·34	19·1 cal.	23·9
CO_2	1·03	1·47	1·51	1·50*	30·6 cal.	20·3
C_2H_2	1·27	1·11	1·41	1·16	32·0 cal.	22·7
C_5H_{12}	1·345	3·59	4·83	4·83*	115·0	23·8
$CH_3.CHO$	1·05	1·88	1·97	2·17	56·0	28·4
$(C_2H_5)_2O$	1·29	3·40	4·39	4·45	104·0	23·7
$CH_3.Br$	1·02	2·09	2·13	—	55·0	25·8
$C_2H_5.Cl$	1·18	2·36	2·78	3·24	69·0	24·8
CCl_4	—	—	5·28†	5·28*		

* These values were used to find the atomic ionisations C = 0·3, H = 0·28, N = 0·5, O = 0·45, Cl = 1·24.

† Bragg, 'Trans. Roy. Soc. South Australia,' vol. 30, 1906. This gives for the atomic ionisation Cl = 1·24.

I wish to express my indebtedness to Prof. J. J. Thomson for having suggested this investigation, and for his kind and inspiring interest.

On the Ionisation of Various Gases by α-, β-, and γ-Rays.

By R. D. KLEEMAN, B.Sc., 1851 Exhibition Research Scholar of the University of Adelaide; Emmanuel College, Cambridge.

When an ionising agent traverses a gas, the ionisation between two parallel planes separated by a distance δx is measured by $K \cdot \delta x$, where K denotes the ionisation per cubic centimetre when it is ionised throughout by an intensity of the ionising agent equal to that between the planes. In order to obtain values of K in practice, the gases under investigation are reduced to such low pressures that they absorb only a small fraction of the energy of the ionising agent, and a set of readings with different gases then gives their respective values of K for the intensity of the ionising agent where it enters the ionisation chamber. A test that the absorption of energy in the gas is small is that the ionisation is directly proportional to the pressure. Strutt[*] has carried out a set of experiments on the ionisation of a number of gases by α-, β-, and γ-rays.

This paper gives the ionisation of a larger number of gases for these rays and the conclusions which may be deduced from the results of the experiments. Let us first consider the α-particle.

§ 1. The α-particle, as the experiments of Prof. Bragg and the writer have shown, is a better ioniser towards the end of its course than at the beginning. We must, therefore, compare the ionisations in different gases for the same velocity of the α-particle. If x is a distance along the course of an α-particle measured from where it enters a gas, and L is its complete range, then, if the ratio L/x is kept constant when dealing with a number of gases, the velocity of the α-particle is the same at the end of each distance x whatever the nature or pressure of the gas. This follows from the fact that since a slab of matter cuts the range of the α-particle down by very approximately the same amount in whatever part of the path it may be placed, the ratio of the range of an α-particle in one gas to that in another gas is independent of the initial velocity of the α-particle. Therefore, the distances in various gases at the end of which the α-particle has the same velocity are given by $(L-x)/L = $ const., that is $L/x = $ const. But the sets of relative ionisations, each of which is taken with a different velocity of the α-particle, will be different unless the ionisation along the course of an α-particle is

similar in all gases, that is, unless the ratio of the ionisation at the distance x_1 to that at the distance x_2 in a gas, where $L/x_1 = K_1$, $L/x_2 = K_2$, and K_1, K_2, denote constants, is the same for all gases.

Prof. Bragg[*] has compared the ionisations along the course of an α-particle in some gases and found them approximately similar, and this is therefore probably true in general. Thus the relative ionisations in various gases for the same velocity of the α-particle are independent of the magnitude of the velocity of the α-particle.

Therefore, if T and I denote respectively the total ionisation and ionisation per cubic centimetre of a gas in terms of air as the standard, and S denotes the stopping power of a molecule of the gas in terms of that of an air molecule, then $1/S$ is the range of an α-particle in the gas in terms of its range in air, and the relation between the qualities T, I, and S is given by

$$ST = I. \qquad (1)$$

Let us assume that it requires the same amount of energy to make an ion from an atom, whether it is free or combined with other atoms. Let T_a denote the total number of ions that would be made by an α-particle in a gas whose molecules consist of atoms a, and T_b the total number that would be made in a gas whose molecules consist of atoms b, so that, if the energy of the α-particle is denoted by unity, the respective energies required to make an ion from each of the atoms a and b are $1/T_a$ and $1/T_b$. Let S_a and S_b respectively denote the stopping powers of the atoms a and b in terms of that of an air molecule. Then, if we have a gas whose molecules consist of N_a atoms a combined with N_b atoms b, the stopping power of this gas will be $N_aS_a + N_bS_b$, and the range of an α-particle in terms of its range in air at the same pressure will be $1/(N_aS_a + N_bS_b)$.

The average amount of energy expended by the α-particle along a length of path in the gas equal to the complete range of the α-particle in air is, therefore, $N_aS_a + N_bS_b$, and therefore the respective amounts of energy expended on the atoms a and b are N_aS_a and N_bS_b. The respective amounts of energy expended along the whole path of the α-particle on the atoms a and b are therefore $\dfrac{N_aS_a}{N_aS_a + N_bS_b}$ and $\dfrac{N_bS_b}{N_aS_a + N_bS_b}$.

The total ionisation, T_{ab}, of the α-particle in the gas is, therefore, given by

$$T_{ab} = \frac{N_aS_a}{N_aS_a + N_bS_b} \bigg/ \frac{1}{T_a} + \frac{N_bS_b}{N_aS_a + N_bS_b} \bigg/ \frac{1}{T_b},$$

that is by

$$T_{ab} = \frac{T_aN_aS_a + T_bN_bS_b}{N_aS_a + N_bS_b}. \qquad (2)$$

* 'Trans. Roy. Soc. of South Australia,' Oct., 1906.

Writing this value of T_{ab} for T in equation (1) and $N_a S_a + N_b S_b$ for S, we get

$$I_{ab} = T_a N_a S_a + T_b N_b S_b. \tag{3}$$

From the manner in which equations (2) and (3) were obtained, it will be readily seen that, in general, if the molecules of a gas consist of atoms $a, b, c, \ldots$

$$T_{abc\cdots} = \frac{T_a N_a S_a + T_b N_b S_b + T_c N_c S_c + \cdots}{N_a S_a + N_b S_b + N_c S_c \cdots} \tag{4}$$

and

$$I_{abc\cdots} = T_a N_a S_a + T_b N_b S_b + T_c N_c S_c + \cdots. \tag{5}$$

Now, $T_a S_a$ is the ionisation per cubic centimetre in a gas whose molecules consist of atoms a, in terms of air as the standard, and $T_b S_b$ the ionisation per cubic centimetre in a gas whose molecules consist of atoms b, etc. (See equation (1).)

Therefore, if the assumption made in the beginning is true, the ionisation in a complex gas must be an additive property of the constituent atoms.

The ionisation values of a number of gases are given in the fifth column of Table I. A large number of these are taken from a paper by Prof. Bragg.[‡]

Table I.

	Atomic ionisation per c.c.	Atomic total ionisation.	Gas.	Experimental ionisation per c.c.	Calculated ionisation per c.c.	Experimental total ionisation.	Calculated total ionisation.	Calculated density of gases.
H	0·175	1·33	Air	1·00	1·00	1·00	1·00	1·00
C	0·51	1·12	O_2	1·15	1·10	1·09	1·04	1·11
N	0·47	0·952	CO_2	1·59	1·61	1·08	1·09	1·53
O	0·55	1·04	CH_4O	1·74	1·76	1·22	1·23	1·11
S	1·24	1·66	C_2H_2	1·40	1·37	1·26	1·26	0·903
Cl	1·16	1·48	C_2H_4	1·73	1·72	1·28	1·28	0·972
Br	1·72	1·46	C_2H_6O	2·46	2·62	1·23	1·31	1·60
I	2·26	1·52	$C_4H_{10}O$	4·40	4·34	1·32	1·30	2·57
			C_6H_6	4·30	4·11	1·29	1·23	2·71
			C_6H_{12}	4·85	4·65	1·35	1·30	2·50
	Atomic stopping power.	Energy spent per ion.	C_2H_4O	2·14	2·27	1·17	1·24	1·53
			N_2O	1·53	1·49	1·05	1·02	1·53
			C_2N_2	1·94	1·96	—	—	1·81
H	0·132	0·754	CH_3I	3·43	3·29	1·33	1·28	4·93
C	0·456	0·894	C_2H_5I	4·00	4·15	1·28	1·33	5·42
N	0·493	1·05	$CHCl_3$	4·08	4·16	1·29	1·32	4·15
O	0·530	0·962	C_2H_5Cl	3·12	3·05	1·32	1·29	2·24
S	0·745	0·603	CCl_4	5·28	5·15	1·32	1·29	5·35
Cl	0·785	0·676	CS_2	2·99	2·99	1·37	1·37	2·64
Br	1·18	0·685	CH_3Br	2·75	2·75	1·32	1·32	3·30
I	1·48	0·658	SO_2	2·01	2·34	—	—	2·22
H*	—	1·10	NH_3	0·81	0·99	—	—	0·590
			H_2	0·24	0·35	—	—	0·0694
			H_2†	0·226				

who obtained them by measuring the ionisation of a certain point along the course of a bundle of α-rays. The value for NH_3 was obtained by multiplying the total number of ions made in NH_3, as found by Laby,* by the calculated stopping power (equation (1)), while the others, with the exception of C_2N_2, were obtained by the writer, using the same method as Prof. Bragg. The value for C_2N_2 is taken from Strutt's paper, and I have also placed his value for H_2 under H_2† in the table. The method used by Strutt is not altogether unobjectionable in the light of more recent knowledge of the properties of the α-particle, unless special precautions are taken, but still his values, with the exception of $CHCl_3$, agree fairly well with those obtained by Prof. Bragg for the same gases.

The ionisation is approximately an additive quantity. If the atomic ionisation values given in the second column of the table are used to calculate the ionisations of the various gases, the values given in the sixth column are obtained. The agreement between the experimental and calculated values, omitting SO_2, NH_3, and H_2 for the present, is as good as can be expected.

This shows then, that the assumption made in the beginning is so far true, and that, therefore, the amount of energy necessary to make an ion from an atom of these gases is independent of chemical combination. It should be observed that from the existence of an additive ionisation law alone it does not follow that the energy spent to make an ion from an atom is independent of chemical combination. For the total number of ions made by an ionising agent, when its energy decreases from e_1 to e_2, depends, besides the intensity of ionisation along its course, on the distance traversed during this change of energy.

If we divide the atomic ionisation of an atom a, that is, $T_a S_a$, by the stopping power of the atom in terms of that of an air molecule, we get T_a, the atomic total ionisation (see equation (5)), and the reciprocal of this gives the energy necessary to make an ion from an atom a in terms of an atom of an air molecule as the standard. The stopping powers of the atoms occurring in the gases given in Table I have been calculated by the square root law from the atomic weights, taking the atomic weight of the standard air atom as 14·4, and are given in the lower part of the second column. The atomic total ionisation and energy necessary to make an ion from an atom, calculated from the second column, are given in the third column.

It will be seen that the α-particle spends the least amount of energy per ion when sulphur atoms are ionised, and the greatest amount when nitrogen atoms are ionised. The expenditure of energy by the α-particle on atoms of

* 'Pass. of Electr. through Gases,' by Prof. J. J. Thomson, new edition, p. 369.

the same kind in a gas consists in ionisation, collision, etc., the sum total of the energy expended being proportional to the square root of the atomic weight of an atom. It does not follow, therefore, that the α-particle finds it really easier to ionise a sulphur atom than a nitrogen atom ; all we can say is that the total expenditure of energy per ion is less with the sulphur atom.

The gases NH_3, H_2, SO_2, especially H_2, show deviations from the additive law, the calculated being greater than the experimental values, and I have not tried to bring them into a line with the other gases, because these gases show similar deviations with other ionising agents. Thus the chemical bond affects the ionisation per cubic centimetre in these gases. If the stopping powers of these gases follow the square root law, the energy spent on any one of their atoms is the same as when it occurs in any of the other gases. The stopping power of H_2 has been determined and was found to be normal,[*] and therefore the α-particle spends more energy per ion when made from a hydrogen atom of a molecule of H_2 than from a hydrogen atom of a molecule of any of the other gases. Thus the chemical bond affects not alone the ionisation per cubic centimetre in H_2, but also the energy spent per ion, and this is probably also true for NH_3 and SO_2. The energy spent per ion of a H atom, when it occurs in H_2, is given under H[*] in Table I.

In the seventh column of Table I, the experimental values of the total ionisation are given for some of the gases. The greater number of these are taken from Professor Bragg's paper. The equations (4) and (5) may be used to calculate the total ionisation and the ionisation per cubic centimetre of a gas obeying the additive ionisation law and the square root law for the stopping power. The total ionisation values calculated by equation (4) are given in the eighth column of the table. For the denominator of the fraction in equation (4), which is the stopping power of the gas, I have used the experimental value of the stopping power[†] instead of calculating it from the atomic stopping powers given in the second column, because this gives a better agreement between the calculated and experimental total ionisation.

It may be mentioned that Prof. Bragg has shown[‡] that the ionisation per cubic centimetre in a gas, denoted by ks in his paper, is approximately proportional to the molecular volume of a molecule. The experiments on the ionisation of various gases by γ-rays will now be described.

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[*] Bragg and Kleeman, ' Phil. Mag.,' Sept., 1905.

[†] Bragg and Kleeman, ' Phil. Mag.,' Sept., 1905, and Bragg, ' Trans. Roy. Soc. of South Australia,' vol. 30, p. 1.

[‡] *Loc. cit.*

§ 2. Fig. 1 is a sketch of the apparatus and their arrangement in these experiments. A is the ionisation chamber, the outside case of which was connected to a potential of 200 volts. It was of a cylindrical form and had a height and diameter of 10 and 9 cm. respectively. The electrode B was connected to an electrometer of the Dolezalek type. The source of γ-rays was a quantity of radium placed at such a distance from the chamber that a convenient leak was obtained, which used to be about 200 mm. divisions in ten seconds. The process of filling the ionisation chamber with pure vapour of some liquid was as follows:—The stop-cock *a* was opened and *b* closed, and the chamber, together with the glass flask C, exhausted by means of
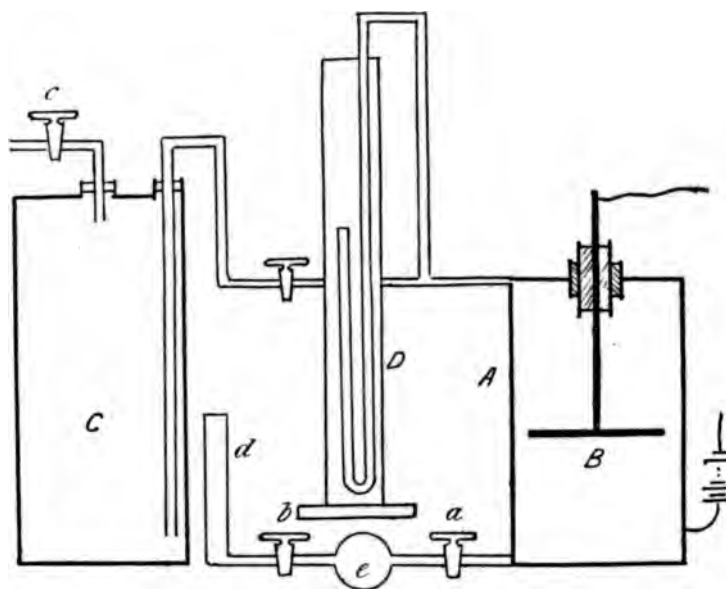
Fig. 1.

a Fleuss pump till the pressure, indicated by the mercury gauge D, was a few millimetres, when the stop-cock *c* was closed. Some of the liquid was then poured into *d*, and by opening the stop-cock *b* part of the liquid was allowed to run into the catch *e*, and evaporisation allowed to go on till the desired vapour-pressure was reached, when the stop-cock *a* was closed. Care was taken that the pressure of each vapour was not too near that necessary to produce condensation. The air which was not removed from the ionisation chamber by the pump was swept by the stream of vapour into the flask C, whose capacity was about ten times that of the ionisation chamber. When the standard air leak was taken, the pressure was always so arranged that the leak was about equal to that of the vapour, in order to avoid the error introduced by the change of capacity of electrometer with the deflection.

The first and second swing of the electrometer needle, when the current was broken, were usually read, and the position of rest of the needle calculated by the formula given in a paper[*] by the writer.

With some of the vapours (CS_2, CCl_4, etc.) the pressure in the ionisation chamber gradually decreased, but ultimately reached a steady state. This was probably due to some chemical action between the vapour and the rubber washers and tubing and the brass case. The leak also as a rule decreased, although corrected for the decrease of pressure, and ultimately reached a steady state. In order to avoid this disturbing effect, the ionisation chamber was first filled with vapour at a lower pressure than that at which the ultimate readings were taken, and allowed to stand for one or two minutes. The vapour was then swept into the vessel C by fresh vapour, and the readings rapidly taken. In this manner very consistent readings were obtained. But the ionisation values obtained for some of the vapours were considerably greater than those obtained by Strutt. The reason for this probably is that Strutt used a very weak source of γ-rays, and therefore had to extend a single reading over a considerable time, during which the vapour may have become more or less impure. It is also of importance to secure pure chemicals; the writer used Kahlbaum's.

The ionisation values of a number of gases, in terms of air at the same pressure as the standard, are given in the eighth column of Table II. Each value, with a few exceptions, is the mean of three separate determinations given in the preceding three columns. The ionisation current was smaller with each vapour than that obtained with air at a pressure of 75·23 cm. of mercury, and when leaks were taken with air for the pressures 75·23, 53·63, 34·94, 14·10 cm., and reduced to correspond to the pressure 75·23 cm., the numbers 2003, 2018, 2009, 2060, were obtained, which show that the ionisation was proportional to the pressure, in this case with air and, therefore, also for the gases.

The ionisation of a gas by γ-rays is an additive property of the atom. The ninth column of the table contains the ionisation values calculated from the atomic ionisations given in the second column. The agreement between the experimental and calculated values is very good, with the exception of H_2, SO_2, NH_3, the calculated values being in their case, as with the a-rays, greater than those given by experiment. Strutt's value for H_2, given in the table under H_2[†], agrees fairly well with my own. Thus the chemical bond in these gases diminishes the ionisation by γ-rays also. The atomic ionisations are roughly given by the equation

$$I = 0\cdot11 + 0\cdot035 \times w, \tag{6}$$

[*] 'Phil. Mag.,' p. 276, Oct., 1906.

where w denotes the atomic weight. The ionisations in the third column of the table are calculated from this equation.

Table II.

	Atomic ionisation.	Ionisation from equation (6).	Gas.				Ionisation per o.o.	Calculated ionisation per o.c.	Calculated density of gases.
H	0·18	0·145	Air	—	—	—	1·00	1·00	1·00
C	0·46	0·53	O_2	—	—	1·16	1·16	1·16	1·11
N	0·45	0·60	CO_2	—	—	1·58	1·58	1·62	1·53
O	0·58	0·67	C_2H_4O	2·15	2·17	2·19	2·17	2·22	1·53
S	1·60	1·23	C_5H_{12}	4·45	4·53	4·61	4·53	4·46	2·50
Cl	1·44	1·33	CH_4O	1·74	1·79	1·73	1·75	1·76	1·11
Ni	1·82	2·07	$C_4H_{10}O$	4·33	4·18	4·36	4·29	4·22	2·57
Br	2·81	2·91	C_6H_6	3·93	3·94	3·95	3·94	3·84	2·71
I	4·50	4·57	C_2N_2	—	—	—	1·71	1·82	1·81
			N_2O	—	1·54	1·55	1·55	1·48	1·53
	Total atomic ionisation.	Energy spent per ion.	C_2H_5Cl	3·18	3·21	3·19	3·19	3·26	2·24
			$CHCl_3$	4·92	4·90	4·97	4·93	4·96	4·15
			CCl_4	6·37	6·38	6·25	6·33	6·22	5·35
			CS_2	3·64	3·68	3·66	3·66	3·66	2·64
			CH_3Br	3·73	3·82	3·88	3·81	3·81	3·30
			C_2H_5Br	4·66	4·66	4·58	4·63	4·63	3·78
H	5·18	0·193	CH_3I	5·35	5·41	5·32	5·37	5·50	4·93
C	1·10	0·909	C_2H_5I	6·56	6·37	6·47	6·47	6·32	5·42
N	0·926	1·08	$Ni(CO)_4$	—	—	5·98	5·98	5·98	5·94
O	1·04	0·962	NH_3	0·894	0·898	0·903	0·898	0·99	0·590
S	1·44	0·694	SO_2	2·29	2·26	2·25	2·27	2·76	2·22
Cl	1·17	0·855	H_2	—	—	0·160	0·160	0·36	0·0694
Ni	0·888	1·13	H_2†	—	—	—	0·169	—	—
Br	1·01	0·090							
I	1·02	0·980							
H*	—	0·434							

Experiments on the absorption of γ-rays by various substances show that if the rays are homogeneous the absorption takes place according to an exponential law, the absorption coefficient being proportional to the density of the absorbing substance. If the absorbing substances were distributed in space so that there are always the same number of molecules per cubic centimetre, as is the case with gases at the same pressure, then the absorption coefficient would be proportional to the sum of the weights of the atoms of a molecule, and therefore an additive quantity.

Let us suppose that the γ-rays do not spread out along their course. Let T denote the total ionisation in a cylinder of gas of 1 cm. cross-section and infinite length in terms of the total ionisation in a similar cylinder of air, the axes of the cylinders being parallel to the direction of the rays. Let λ denote the absorption coefficient, and I the ionisation per cubic centimetre

where the rays enter the cylinder, in terms of air at the same pressure as the standard.   Then

$$T = I \int_0^\infty e^{-\lambda x} \, dx,$$

and therefore $T = I\lambda.$ (7)

We have thus a similar equation connecting the total ionisation, the absorption and the ionisation per cubic centimetre, in the case of γ-rays to that which obtains in the case of α-rays.   Since λ can be calculated, being in a given case equal to the molecular weight of the gas divided by that of air, and I calculated by means of the atomic ionisations given in the second column of Table II, we can obtain from equation (7) the total ionisation by γ-rays in a given gas, a quantity that will scarcely be ever determined directly, but only by some indirect method such as this.   The calculated total ionisation values for a number of gases are given in the second column of Table III, and in the third column the experimental values of the total ionisation by the α-particle are placed for comparison.   It will be seen that the values, like those of the α-particle, all lie between the numbers one and two.

Table III.

Gas.	Calculated total γ-ionisation.	Experimental total α-ionisation.
Air	1·00	1·00
O_2	1·04	1·09
CO_2	1·03	1·06
C_2H_4O	1·42	1·17
C_5H_{12}	1·81	1·35
CH_4O	1·56	1·22
$C_4H_{10}O$	1·67	1·32
C_6H_6	1·45	1·29
N_2O	1·01	1·05
C_2H_5Cl	1·42	1·32
$CHCl_3$	1·19	1·29
CCl_4	1·18	1·32
CS_2	1·39	1·37
CH_3Br	1·16	1·32
CH_3I	1·09	1·33
C_2H_5I	1·19	1·28

We can deduce from equation (7) two equations similar to the equations (4) and (5) relating to the α-particle.   When the energy of an α-particle decreases from e_1 to e_2 in a gas, the distance traversed is equal to the reciprocal of the sum of the square roots of the weights of the atoms of a molecule multiplied by a constant, this constant being the same from gas to gas if they are at the same pressure.   In the case of γ-rays, the distance

traversed during which their energy decreases from e_1 to e_2 is given by $e_1 e^{-\lambda x} = e_2$, that is by $x = \dfrac{1}{\lambda} \log \left(\dfrac{e_1}{e_2} \right)$. Since $\log (e_1/e_2)$ is constant, the distance traversed in a gas is inversely proportional to the sum of the atomic weights of a molecule. Thus λ may be called the stopping power of a gas with respect to γ-rays. Therefore, if we introduce the quantities atomic ionisation and atomic total ionisation, and assume that the amount of energy spent by the γ-rays to make an ion from an atom is independent of chemical combination, we can, as is obvious, deduce two similar equations as (4) and (5) for the γ-rays. Thus we see that, if the ionisation by γ-rays follows an additive law for some gases, then the above assumption, that the energy spent per ion per atom is independent of chemical combination, is true for these gases.

The total atomic ionisation and the energy spent per ion per atom, obtained in a similar way to the same quantities for the α-particle, are given in the lower parts of the second and third columns of Table II. It will be seen that in the case of the atoms given in the table, the γ-rays spend the least amount of energy per ion when ionising hydrogen atoms and the greatest amount when ionising nickel atoms, nitrogen atoms coming next. The α-particle, it will be remembered, spends the least amount of energy per ion when ionising sulphur atoms. As pointed out in the case of the α-particle, it does not follow that the ionisation must necessarily account for all the energy expended. If each of the coefficients of absorption of the gases SO_2, NH_3, H_2 is proportional to the sum of the weights of the atoms of a molecule, as it has been taken to be in the case of the other gases, then the γ-rays spend more energy per ion made from an atom when it occurs in these gases than when it occurs in any of the others. Assuming the absorption coefficient of H_2 to be normal, the energy spent per ion of an atom of H when it occurs in H_2 is given under H* in the table.

The experiments on ionisation by γ-rays are complicated by the fact that the walls of the ionisation vessel give off secondary cathode rays which possess ionising power themselves. It will be seen afterwards that the β-ray ionisation is almost exactly the same as that obtained for the γ-rays, therefore, if the ionisation by these secondary rays were of some magnitude, and the γ-ionisation values were different from the β, this would not be the case. Thus we conclude that, whether the ionisation was appreciably affected by these secondary rays or not, the numbers in the table represent the γ-ionisation in the various gases. We will now describe the experiments made with β-rays.

§ 3. The apparatus used and their arrangement in the experiments with the

β-rays are shown in fig. 2.   H is the ionisation chamber.   A flat circular dish k of diameter 10·5 cm., and having a small hole in the bottom, contained uranium oxide, which was moistened when put into the dish and then allowed to dry, becoming a solid cake.   The dish, in order to cut off the a-particles, was covered with aluminium foil bent down at the side, and held
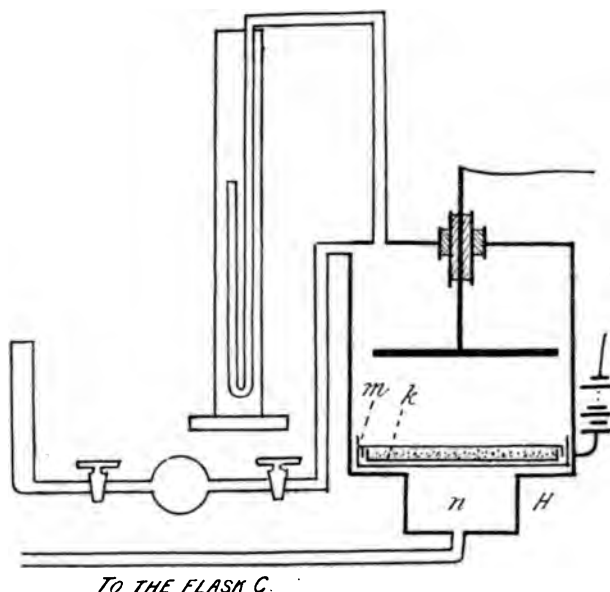
Fig. 2.

down by brass cross-pieces soldered to a similar but larger dish m, into which k was placed.   The distance of the aluminium foil from the electrode was 5 cm.   It will be seen from the diagram that the motion of the air or vapour, during exhaustion or the letting in of vapour, was always such that if any uranium particles· were carried along by the current of gas, they would be swept into the compartment n, and thus would not affect the β-leak.   The leak, when the chamber was full of air at atmospheric pressure, was about 63 mm. divisions of the scale in 10 seconds.

The β-ionisation values of the gases in Table II are given in the sixth column of Table IV.   Leaks were taken with air for the pressures 15·82, 35·57, 56·12, 77·57 cm. of mercury and reduced to a pressure of 77·57 cm., and the numbers 2430, 2396, 2340, 2400 obtained, which show that the ionisation was proportional to the pressure.   The leaks with the gases in the table were generally smaller than that of air at atmospheric pressure, and therefore the ionisation must have been approximately proportional to the pressure in the neighbourhood of the pressures used.

Table IV.

	Atomic ionisation.	Gas.			Ionisation per c.c.	Ionisation per c.c., γ-rays.	Calculated ionisation per c.c.	Calculated density of gases.
H	0·18	Air	—	—	1·00	1·00	1·00	1·00
C	0·46	O_2	1·16	1·19	1·17	1·16	1·16	1·11
N	0·475	CO_2	1·62	1·58	1·60	1·58	1·62	1·53
O	0·58	C_2H_4O	2·10	2·14	2·12	2·17	2·22	1·53
S	1·60	C_5H_{12}	4·50	4·61	4·55	4·58	4·46	2·50
Cl	1·44	CH_4O	1·67	1·71	1·69	1·75	1·76	1·11
Br	2·67	$C_4H_{10}O$	4·44	4·35	4·39	4·29	4·22	2·57
I	4·10	C_6H_6	3·92	3·98	3·95	3·94	3·84	2·71
		C_2N_2	—	—	1·86	1·71	1·87	1·81
		N_2O	1·55	1·56	1·55	1·55	1·53	1·53
		C_2H_5Cl	3·19	3·30	3·24	3·19	3·26	2·24
		$CHCl_3$	4·88	5·00	4·94	4·93	4·96	4·15
		CCl_4	6·23	6·33	6·28	6·33	6·22	5·35
		CS_2	3·58	3·65	3·62	3·66	3·66	2·64
		CH_3Br	3·70	3·77	3·73	3·81	3·67	3·30
		C_2H_5Br	4·41	4·40	4·41	4·63	4·49	3·78
		CH_3I	5·11	5·11	5·11	5·37	5·10	4·93
		C_2H_5I	—	5·90	5·90	6·47	5·92	5·42
		NH_3	0·885	0·892	0·888	0·898	1·02	0·590
		SO_2	2·25	2·26	2·25	2·27	2·76	2·22
		H_2	—	0·165	0·165	0·160	0·36	0·0694
		H_2*	—	—	0·157	0·169		

The ionisation values obtained with γ-rays are placed in the seventh column for comparison. It will be seen that they are almost exactly the same as those obtained with β-rays, the only appreciable difference occurring with the iodides. The eighth column contains the ionisation values calculated from the atomic ionisations given in second column, the atomic ionisations being the same as those used in the case of γ-rays, except for the atoms N, Br, and I, but the atomic ionisations of I only differ appreciably from one another.

An interesting deduction can be made from the additive ionisation law. Since the ionisation is independent of chemical combination, the number of electrons lost by an atom is a constant which is independent of chemical combination, but which may vary with the kind of atom. Now, Townsend's diffusion experiments, as well as the experiments by Prof. Thomson on the charge of an ion, show that the positive and negative ions have equal charges when made by β-, γ-, or X-rays, in air, CO_2, or O_2. Thus the atoms N, O, C lose one electron only when ionised by one of these ionising agents, and not more than one atom of a molecule gets ionised. Therefore, as an example, with CO_2, the ratio of the number of oxygen atoms per cubic centimetre, or molecules in which the oxygen atom is ionised, to the number

of molecules in which the carbon atom is ionised is, in the case of γ- or β-rays, as 2 × 0·58 to 0·46, that is, as 1·16 to 0·46. That the ionised atom loses one electron only is probably true for all kinds of atoms. In the case of the α-particle, there is scarcely any evidence as to the number of electrons lost by an ionised atom. The velocities of the positive and negative ions under an electric force, and other properties, suggest, however, that an atom loses one electron only.

The atomic ionisation for α-, β-, and γ-rays has been plotted against the atomic weight in fig. 3. There is an interesting similarity between the
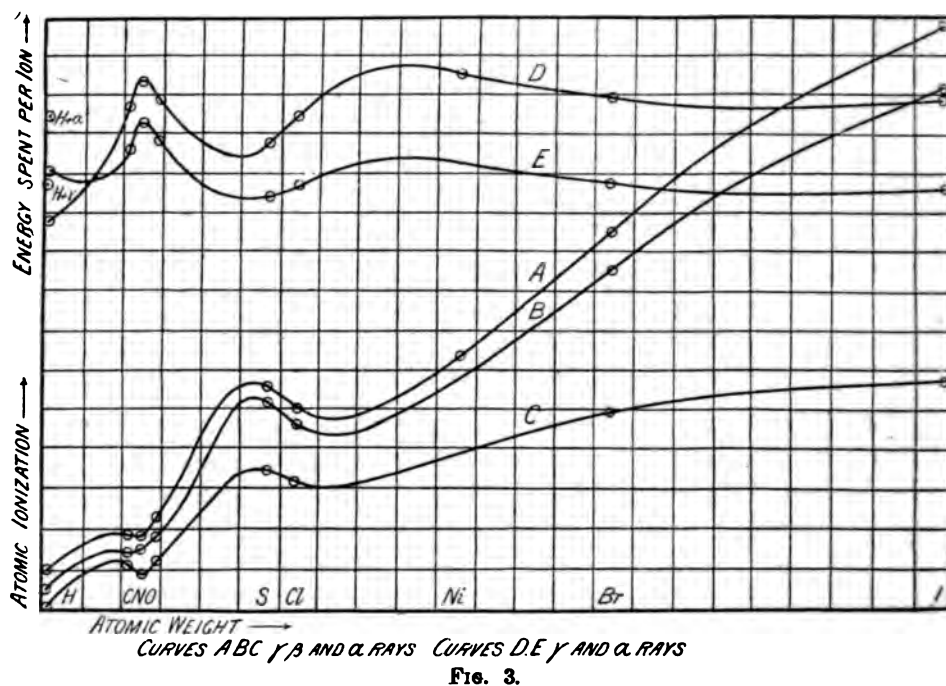
Fig. 3.

curves obtained, shown by two sets of kinks. The curves have been separated somewhat, to prevent overlapping. The ionisation with each ionising agent thus seems to be some periodic function of the atomic weight. The first short period of the periodic classification of the elements is represented by H, C, N, O, the second short period by S, Cl, and the first and second long period by Ni, Br, and I respectively. The similarity between these curves means that similar conditions regulate the chance of a number of atoms getting ionised by one of these ionising agents. And this may be so if the electron is pulled or knocked out of an atom in one case, while an absorption of energy till something like an explosion of the atom occurs takes place in another case ; for, if one gas is more easily ionised than another by the first

process, we should also expect that a smaller amount of energy would be necessary to produce an explosion of an atom of that gas.

The curves D and E in fig. 3 show the relation between the energy spent per ion and the atomic weight for α- and γ-rays. These curves also resemble one another, which means that similar conditions regulate the total expenditure of energy per ion. It should be observed that from the way the energy spent per ion is obtained, it does not follow that if the curves A and C resemble one another, D and E must resemble one another. The numbers representing the energy spent per ion are only relative and, in the case of the α-particle, the absolute amount of energy spent per ion decreases as the α-particle approaches the end of its course. This follows from the fact that the α-particle makes more ions towards the end of its course, while the rate of expenditure of energy all along the course is the same. It appears from the curves D and E and, in the case of the α-particle, also from the foregoing fact, that the energy spent per ion is not connected in a simple way with the atomic weight and, therefore, not connected in a simple way with the absorption of energy. The abnormal behaviour of H_2 with respect to the energy spent per ion per atom and the ionisation per cubic centimetre, in comparison with other gases, is interesting in connection with the abnormal scattering of cathode rays in H_2, which is pointed out and discussed by Professor Thomson.[*]

We have no experimental evidence on the connection of the atomic or molecular weight of a gas with the distance traversed by a β-ray while its energy decreases from e_1 to e_2, say; and therefore we are not able to determine in this case the relative amounts of energy spent per ion per atom, and whether the amount of energy spent per ion is independent of chemical combination.

Strutt showed in his paper that the ionisations by α-, β-, and γ-rays, of the gases examined by him, were nearly proportional to the densities of the gases. But this is accidental; moreover, only a rough approximation to the density is shown by the ionisation values given in this paper, and the law does not hold at all for many of the other gases. This will be evident from comparing the ionisations with the densities of the gases given in the last column of each table.

I have much pleasure in thanking Professor Thomson for his kind interest and ready advice at all times.

[*] 'The Discharge of Electricity through Gases,' p. 382.

On the Explosion of Pure Electrolytic Gas.

By Harold B. Dixon, M.A., F.R.S., Professor of Chemistry, and Lawrence Bradshaw, M.Sc., late Dalton Scholar of the University of Manchester.

[Plates 2 and 3.]

The fact that a large number of chemical reactions have been shown to be dependent on the presence of aqueous vapour has led to many experiments being made on the union of hydrogen and oxygen. Some years ago one of us[*] made experiments which showed that an electric spark would fire ordinary electrolytic gas, whether in the dried or the moist state; and experiments on the rate of detonation in electrolytic gas seemed to show that, once an explosion-wave was started, no influence was exerted on the propagation of the wave by aqueous vapour, except a slightly retarding one.

More recently, H. B. Baker[†] carried out a series of experiments with very pure hydrogen and oxygen obtained by the electrolysis of a solution of highly purified barium hydroxide. His results show that the initiation of the flame by a heated wire is largely influenced by the purity of the gases.

If the interaction of hydrogen and oxygen depends upon the presence of previously formed water molecules, it appeared probable that there might be a difference in the rate at which the flame spread when initiated by a spark in the moist and dried gases.

With a view to finding whether or not there is any such difference, either in the initial stage of the explosion or in the subsequent phenomena, we have made a photographic analysis of the explosion flame in the dried and undried gases. The photographs were taken on a film moving vertically downwards with great rapidity, while the flame, started by a spark between platinum wires in a Jena glass tube, travelled horizontally towards either end.

Experimental Part.—The Jena glass explosion-tubes were cleansed successively with distilled water, a mixture of sulphuric acid and potassium dichromate, and fuming nitric acid, and finally washed with distilled water. After draining, they were dried first in a steam oven and then by heating in a furnace, while at the same time a stream of hot air, filtered through cotton wool and dried by means of P_2O_5, was drawn through them.

Preparation of Pure Materials.—The gaseous mixture was prepared by Baker's method, viz., by electrolysing an aqueous solution of barium

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* H. B. Dixon, 'Phil. Trans.,' 1884, p. 634, and 'Chem. Soc. Trans.,' 1886, p. 108.

† 'Chem. Soc. Journ.,' vol. 81, p. 401, 1902.

Fig. 1.—Dry.

Fig. 2.—Moist.

Fig. 3.—Dry.

Fig. 4.—Moist.

⁎ Figs. 3 (Plate 2) and 5 (Plate 3) do not show the dim lower part of the flame; the original films show them of nearly equal intensity with the same parts in the "moist" gases (figs. 2 and 4, Plate 2).

Fig. 5.—Dry.

Fig. 6.—Moist.

Fig. A.

Fig. B.

hydroxide. For experiments with undried gases, the mixed hydrogen and oxygen were collected directly over mercury in a glass gas holder. For the experiments with dry gas, the mixed gases from the electrolytic cell were roughly dried by passing through two tubes of redistilled P_2O_5, and were collected in a holder over mercury, upon the surface of which rested some P_2O_5. The tubes (each containing a quantity of P_2O_5) were filled from this holder.

The barium hydroxide was obtained by several recrystallisations of Kahlbaum's " pure " $Ba(OH)_2$; it still contained a small quantity of carbonate. The phosphorus pentoxide was redistilled in a stream of dry oxygen over platinised asbestos.

The tubes were washed out several times with the mixed gases and were then sealed with fusible metal (at A in illustration), after which they could be safely drawn off (at B) in the blow-pipe flame.
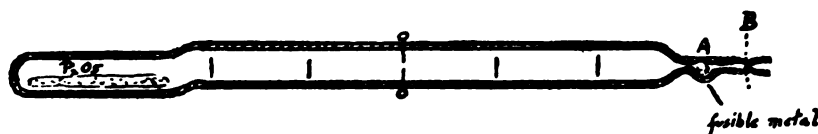
1st Series (July to September, 1902).—Three tubes into which a quantity of P_2O_5 had been introduced were filled with the mixed gases and were allowed to stand in the dark for two months. Three control tubes (moist gases) were prepared at the same time and also left standing. Of these the photographs 1 and 2 (Plate 2) were the most successful; 1 shows the explosion of the dried gases, 2 the moist. They appear to agree in every respect.

A *2nd series*, carried out in the same way, confirmed these results.

3rd Series (April to July, 1903).—To make the conditions more nearly alike, a quantity of finely powdered SiO_2, equal in bulk to the P_2O_5 in the dry-gas tubes, was introduced into the tubes containing the moist gases. The tubes remained in the dark for two and a-half months.

Photographs 4 and 6 (moist) are comparable with 3 and 5 (dry) (Plates 2 and 3). These photographs confirm those of Series I. The effects observed in the moist and in the dry gases are identical. The dark, vertical lines seen on the photographs are caused by thin bands of dark paper gummed on the explosion tubes to serve as reference marks.

Our experiments show that, as far as can be judged from the flame, the absence of water vapour does not influence the explosion of a mixture of hydrogen and oxygen once the flame has been started by a spark.

The Firing of Gaseous Mixtures by Compression.

By Lawrence Bradshaw, M.Sc., Ph.D.

[Plate 3.]

During the course of the experiments described in the preceding paper, in which the movements of the flame in the explosion of electrolytic gas were recorded on a rapidly moving photographic film, we observed a new phenomenon. In addition to the ordinary effects accompanying the explosion,* the photograph showed a new luminous wave advancing from one end of the explosion-tube to meet the flame spreading slowly from the point of origin in the middle of the tube.

As we had not noticed this before in any one of the hundreds of photographs of the explosion-flame taken in this laboratory, we were led to suspect that this spontaneous ignition was caused by the peculiar shape of explosion-tube used for the first time in the above experiments. The electrolytic gas was enclosed in a glass tube, one end of which had been previously drawn out to a fine capillary in the blow-pipe flame, in order to facilitate the sealing of the tube after the gaseous mixture had been introduced. Following the device of H. B. Baker,† the capillary was first closed by allowing a small quantity of molten fusible metal to solidify in it. The end of the narrow tube could then be sealed off with a small flame without fear of the gases being prematurely exploded. One end of the tube was therefore shaped like a funnel (fig. 1, a).
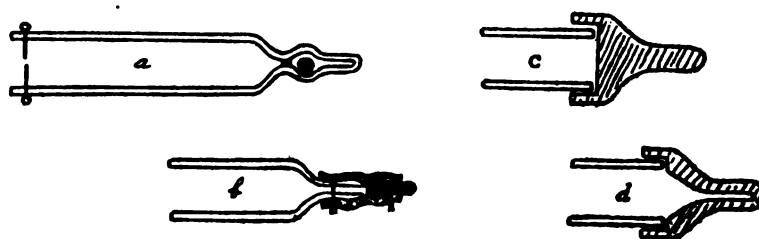
Fig. 1.

The wave in question seemed to originate at this end of the tube. We concluded that the gaseous mixture had fired spontaneously in this region, owing possibly to an invisible compression-wave compressing the gases in the

* H. B. Dixon, "The Movements of the Flame in the Explosion of Gases," 'Phil. Trans.,' vol. 200, p. 315, 1902.

† H. B. Baker, 'Chem. Soc. Journ.,' vol. 81, p. 400, 1902.

funnel to such an extent as to fire the mixture by the heat of compression. In the photographs the exact starting point of the flame cannot be seen; it is obscured by the clamp which held the tube in position.

At the suggestion of Professor H. B. Dixon, I therefore undertook the following research in order to obtain more evidence concerning the origin of the new combustion-wave, and the conditions under which it is set up.

In the experiments described in this paper no fusible metal was used; the capillary was sealed in the blow-pipe flame and the electrolytic gas introduced afterwards from the other end by evacuating the tube and filling it with the gas, the operation being repeated several times to get rid of all the air.

The photographs were taken in the usual way, viz., on a sensitised film stretched round a drum rotating with great rapidity, the film moving vertically downwards on the side nearest the explosion-tube, while the flame travelled in the tube horizontally. Only that portion of the tube between the firing wires and capillary end is shown in the photographs. The broad black band is caused by the clamp; the fine lines are due to narrow strips of paper pasted on the tube at intervals of three inches on each side of the firing-wires, and serve as reference lines. Fig. 2 will make the general arrangement of the tube clear. The spark was passed immediately to the right of the clamp holding the tube, at a distance of $7\frac{1}{2}$ inches from the conical end.
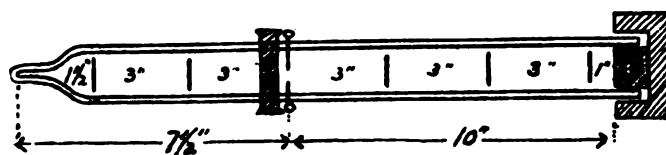
FIG. 2.

Fig. A (Plate 3) shows the movements of the flame in the explosion of $2H_2 + O_2$ in this tube. In the negative the spark may be detected a little to the right of the dark band; the flame spreads with increasing velocity to the right and to the left. When the flame has reached a point midway between the first and second reference lines to the left, *i.e.*, about $4\frac{1}{2}$ inches from the spark, a second flame* appears at the capillary end of the tube and moves forward with a velocity somewhat less than that of the flame initiated by the spark, and in the opposite

FIG. 3.

direction. The two flames meet a little to the right of the first reference
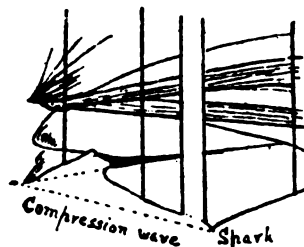
* This flame starts about 1/2700 sec. after the passage of the spark.

mark in the photograph. Fig. 3 is a plan showing, in outline, the movements of the flames.

It will be noticed that the initial flame is checked by a sound wave *reflected* from near the end of the tube.

The phenomenon is more clearly seen in fig. B (Plate 3), a photograph of the intensely bright flame in a mixture of carbon disulphide and oxygen (in the proportion $2CS_2 + 3O_2$) under the same conditions, the only difference being that in this case the spark-gap was 13 inches from the end of the tube; the film moved a little faster than in the previous case.

The same effects were observed in a large number of photographs, which it will not be necessary to reproduce here.

Experiments were made in which the relative diameters of the tube and capillary, and the length of the capillary, were varied, but the result was always the same, viz., the gas always ignited in the narrow portion of the tube. In a second series of experiments the distance between the spark gap and the capillary end of the tube was varied between 3 and 13 inches without affecting the result.

In all these experiments the end of the capillary was closed by sealing in the blow-pipe flame before introducing the explosive mixture.

It was next found that if this end is closed by means of a piece of stout pressure-tubing (wired on) and a piece of glass rod pressed against the orifice (fig. 1, *b*), no firing takes place. In this case the explosion was accompanied by a sharp click, as though the rubber tubing had yielded for an instant to the sudden pressure and then returned to its original position. The tube remained intact after the explosion. In one experiment, in which the glass stopper was pressed very tightly against the opening, the explosion was noiseless, and the gas was ignited in the capillary in just the same way as when this was hermetically sealed. Hence it appears that the new wave can only be set up when the end of the tube is quite rigid. This in itself is strong evidence in favour of the assumption that the gas is fired by compression.

It might be supposed that if an unyielding surface is all that is necessary to ensure spontaneous ignition, the same result could be brought about in a tube of uniform diameter closed with a flat metal plate. Fig. 1, *c*, shows a portion of such a tube. A tightly fitting brass cap was cemented on to the end and held in position by means of a clamp. This withstood the shock of the explosion, but the photograph shows no indication of any firing of the gases by compression, the picture obtained being similar in every respect to those usually obtained in tubes closed with rubber stoppers.

The brass end-piece was next removed from the tube, drilled to the shape shown in fig. 1, *d*, and then replaced on the original tube. This time the wave

was set up in the same manner as when the explosion tube had been drawn out to the same shape in the blow-pipe flame.

It follows .that two of the conditions essential to the setting up of the wave are that the end of the tube must be funnel-shaped and unyielding. The wave produced is analogous to the tidal " bore " in a funnel-shaped estuary.

The distance from the firing-wires to the end of the tube is also important; it must be less than that required for the development of the detonation-wave in the gaseous mixture.

I have calculated the velocity with which a wave would have to travel from its point of origin in order to reach the end of the tube at the instant at which the gas ignites, as judged from the photographs.

The interval of time which elapses between the passage of the spark and the spontaneous inflammation of the gas at a point several inches distant from the firing-wires can be ascertained, when the velocity of the rotating film is known, by measuring on the film the vertical distance between the image of the spark and the image of the flame where it first appears. The amount of displacement is proportional to the time. In these experiments the film moved at the uniform rate of 19·84 metres per second, so that each centimetre, measured vertically, corresponds to about 1/2000 second.

A record was kept of the dimensions of the tubes, but the length from the spark-gap to the end of the tube can easily be estimated from the photographs by remembering that the strips of paper on the tube are 3 inches (7·62 cm.) apart, and the reference marks given by these in the photograph exactly 1 cm.

The rate of propagation of the wave is calculated from the length of the tube and the time taken by the wave to traverse it. I have made the various measurements as carefully as possible, but dealing as we are with velocities of the order of hundreds of metres per second over distances of a few centimetres, it is hardly to be expected that the results obtained in this way will be very concordant. Five of the best photographs of the explosion of $2H_2 + O_2$ were selected and the following data obtained :—

Experiment No.	Distance from spark to end of tube.	Vertical displacement.	Velocity of film in metres per second.	Calculated velocity of compression-wave in metres per second.
	mm.	mm.		
C 1	229	8·5	19·84	533·6
C 3	137	5·5	19·84	494·9
C 14	221	7·0	19·84	604·8
C 16	196	7·2	19·84	539·5
CC 17	111	4·7	19·84	466·5
				Mean 527·9

The mean value for the velocity of the compression-wave was thus found to be 527·9 metres per second.

This approximates closely to the velocity which a sound-wave would have in electrolytic gas under the same conditions, calculated from Laplace's formula, $v = (P\gamma/\rho)^{\frac{1}{2}}$; ρ is the density of the gaseous mixture, and γ the ratio of the specific heat at constant pressure and at constant volume. Substituting in the above equation $P = 1$ atm. (1013300 dyne/cm.²), $\rho = 0.0005364$, and $\gamma = 1.41$, we find $v = 522.1$ metres per second.

Owing to the difficulty of obtaining a trustworthy value of γ for the mixtures of CS_2 with oxygen, the same method of examination cannot be employed. Such mixtures are, however, very valuable for studying the movements of the flame on account of the highly actinic nature of the light produced by them in exploding.

Although the rate calculated for the velocity of the wave which causes the ignition in the case of electrolytic gas agrees fairly well with that of sound in the same gas, it is difficult to believe that the firing is brought about by a sound-wave or series of sound-waves of the ordinary type, when the large amount of energy required to fire the mixture by the heat of compression is considered.

For the temperature of ignition of a mixture of hydrogen and oxygen in the proportion $2H_2 + O_2$, widely different values have been obtained by various observers.[*] Let us take, for the purpose of calculation, the lowest of these, viz., 555° C., given by Mallard and Le Chatelier.[†] The pressure which is necessary to produce this elevation of temperature, if the heating takes place adiabatically, may be calculated from the formula $T'/T = (p'/p)^{\gamma-1}$, where T, T', are the absolute temperatures corresponding with the pressures p and p' respectively, and γ is, as before, the ratio of the specific heats at constant pressure and at constant volume. In the above experiments, $T = 286°$ C., $p = 1$ atmosphere, $\gamma = 1.41$, and it is found that the least pressure which will suffice to ignite the mixture is 13½ atmospheres.

Whatever the nature of the wave under discussion, it may be overtaken and destroyed by a detonation-wave when the latter is allowed to have a sufficient run. This is shown by the following experiment. A leaden pipe about 4 feet long was attached to a glass tube used in one of the earlier experiments, at the end furthest from the capillary. When the mixture is fired by a spark at the extreme end of this pipe, the wave of chemical combustion, slower at the start than the physical wave which precedes it, constantly increases its rate of propagation until it assumes the enormous

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* See J. W. Mellor's 'Chemical Statics,' p. 447.

† 'Recherches sur la Combustion des Mélanges Explosifs,' Paris, 1883, p. 88.

velocity of the true detonation-wave. The detonation gains rapidly on the compression-wave and ultimately catches it up and absorbs it. The photograph shows that, under these circumstances, the gas is not fired in the capillary before the detonation-wave reaches it.

As far as the evidence goes, it seems to support the view that the spontaneous inflammation of a gas, under the conditions described in this paper, is caused by a wave of compression moving with about the same velocity as that of a sound-wave.

On the Thermo-chemistry of Flame Spectra at High Temperatures.

By W. N. HARTLEY, F.R.S., D.Sc., Royal College of Science, Dublin.

The majority of the metallic elements have two distinct spectra, one of lines, the other of bands. In some spectra, bands are the most prominent feature in association with but few lines; in others the lines predominate over the bands. Of those substances with bands in their spectra there are many which may be reduced in quantity to almost a minimum without the bands disappearing from the flame or from the uncondensed spark; from this it would appear that there is a very intimate relationship between the bands and lines of the same element. It has been supposed that such bands as cannot be attributed to definite salts are the spectra of oxides or even of hydrides, but many facts have been accumulated from which it is evident that this is not correct. On the other hand, many of the elements which possess complex molecules may readily be understood to emit molecular or band spectra, but some further explanation is necessary when the molecule of the element is monatomic.

The present communication deals only with one part of this subject, being merely a record of observations on high temperature flame reactions, and principally those of the alkali and alkaline earth metals. The spectra of the alkali metals at the highest temperature in the flame of the oxyhydrogen blow-pipe more nearly resemble those obtained from the arc than any other spectra of the same elements. Thus, all the lines of lithium photographed by Kayser and Runge in the arc have been obtained in the flame from lithium nitrate. This is evidence of the high temperature obtainable in the flame, but if further evidence were desired, we have it in the great facility with which both gold and silver can be vapourised and condensed from the vapour, the large number of arc lines of iron, practically all those that are reversible, which appear in the flame, and the volatilisation of palladium and iridium in weighable quantities.

Part I.—BAND SPECTRA OF THE ALKALI AND ALKALINE EARTH METALS.

Lenard[*] has recently described the coloured glow emitted by globules of fused salts in the Bunsen flame, the particular parts of the flame from

[*] 'Annalen der Physik,' 1905 (IV), vol. 17, pp. 197—247.

which the glow emanates, with the spectrum of the glow from different metals.

The spectra of the glow from metallic vapours have been photographed repeatedly in the oxyhydrogen flame spectra of all the alkali metal salts,[*] and those of the alkaline earths, but Lenard states that he has not been able to find the maximum of brightness of the continued rays of potassium, at or near λ 5500, as it appears on the reproduction of my photographs (Plates 6 and 7). On referring to the plate, I do not see that the maximum is at λ 5500, and the strong continuous rays are so evenly distributed over so wide a range of spectrum that it is better to refer to the letterpress of the publication.

The continuous spectrum of lithium extended from about λ 4600 to λ 3200; of sodium very strongly from λ 6020 to λ 3600 and continued weakly to λ 3320; of potassium it was intense from about λ 4600 to λ 3400, but continuous rays were observed from about λ 5700. As importance has been attached to the kind of photographic plate used, it is as well to state that isochromatic plates of Edwards', or of the Ilford make, and Cadett and Neall's spectrum plates, were most generally in use, but when the plates were not isochromatic, the fact was recorded on the photograph. On the photograph referred to by Lenard, the plate was less sensitive to the green than to the orange and red rays, so that a weak space is seen between λ 5359 and λ 5200. The continuous spectra have been carefully examined on more than 40 different photographs of the alkali-metal salts, including sulphates, nitrates, carbonates, and chlorides; also potassium cyanide, ferrocyanide, ferricyanide, and fluosilicate.

A hitherto undescribed feature in the spectra which is unquestionably due to each metal, is the occurrence of a multitude of bands in the rays of lithium, sodium, and potassium, which occupy spaces within the above-quoted wave-lengths.

The photographed spectra of potassium chloride, as emitted by different flames, were studied. In no case did the nature of the salt, the support used, or the nature of the flame, make any difference, except in lengthening or shortening the exposure which, *during comparatively short periods*, was proved to have the same effect as putting more or less of the salt into the flame.

It is deemed of importance that this should be recorded, because different metals, and also different salts of the same metal, under the same conditions show different results, and this arises principally from the difference in

volatility of the salts, or the comparative ease with which they are thermo-chemically decomposed. It is also important that the salts be pure, otherwise the spectrum of one may interfere with the other, the two spectra become confused, and the bands are not visible.

Lithium Salts.—Various specimens of the sulphate, carbonate, chloride, and nitrate, were used, but most of the spectra were photographed from the nitrate. Latterly the salts obtained have been so pure that the sulphate showed hardly a trace of any other metal, even sodium, and no calcium.[*] They show all the lines attributed to lithium by Kayser and Runge. The structure of the background is that of fine lines and very narrow bands extremely close together, extending from $\lambda 3466$ to $\lambda 4677$. But it must be observed that a feeble group of the water-vapour lines may be seen on other spectra extending to $\lambda 3466$, therefore to be sure that these may not be mistaken for lithium bands, it is better to place the margin of the latter below $\lambda 3610$ and to disregard the rays of greater refrangibility. The lithium bands, therefore, without doubt, extend from $\lambda 3610$ to $\lambda 4677$. The lithium spectrum, exclusive of the lines, is a very weak one, so that an extended band of continuous rays is more often photographed than a discontinuous spectrum consisting of a multitude of fine lines and narrow bands.

Sodium Salts.—The banded spectrum of sodium has been observed on three photographs, but it is only feebly visible. A complete array of the bands was photographed from very pure rock salt, and from a specially prepared pure sodium chloride. Like the lithium bands, they are very narrow and close together; they extend from rays a little less refrangible than $\lambda 3700$ down to about $\lambda 4800$. A beautiful banded spectrum has recently been photographed from sodium carbonate in the oxyhydrogen blow-pipe flame. Some feeble lines accompany the bands, and the principal lines D^1 and D^2 are enormously extended on each side so as to form a broad band. O. H. Basquin observed a series of lines in the spectrum of the sodium arc when surrounded by an atmosphere of hydrogen; they lie between $\lambda 5000$ and 3800.[†] "This is probably a complicated fluting of heads of bands, less clearly marked than usual, and running towards shorter wave-lengths." It is more than probable that the bands which I have observed are of the

* These salts were kindly presented to me by Mr. W. E. B. Blenkinsop, the Managing Director of the firm of May and Baker, Ltd., of Garden Wharf, Battersea, London.

† 'Astrophys. Journ.,' 1901, vol. 14, p. 1. In lieu of any better hypothesis, Basquin supposed that the banded spectra of several of the metals, including sodium, are due to hydrides being formed in the arc. Sodium hydride cannot exist in a state of vapour; it readily undergoes dissociation, which commences at 200° and is complete at 422°, under ordinary barometric pressures; the bands, therefore, are not due to sodium hydride.

same nature as those which he, by the aid of a large concave grating, resolved into lines.

There is an important difference between the spectrum of sodium taken from the metal when burnt in a Bunsen flame and that obtained in the oxyhydrogen blow-pipe flame, but it appears to be due solely to the lower temperature of the former. With metallic sodium, no lines but the principal yellow ones are visible, these are very broad and dense. It is extremely difficult to introduce sodium into the oxyhydrogen blow-pipe flame, because it melts so readily and escapes. The sodium spectrum from salts gives not only the D^1 and D^2 lines more widely extended on either side than is the case with the metal, but also the subordinate series of lines, the band of continuous rays, and with the highest temperature of the flame, the series of bands in these rays in addition.

Potassium Salts.—The potassium bands are very easily photographed from many different salts. They are themselves wider, and also wider apart than those of lithium and sodium, and the structure of the banded spectrum varies greatly with the quantity of the substance used, and with the exposure given. Many lines accompany the stronger banded spectrum.

The potassium bands, as obtained from weighed quantities of potassium chloride, frequently extend from $\lambda 3600$ to $\lambda 4800$. This effect is obtained from 0·05 gramme of the salt, but with 1 gramme or an exposure of 5 minutes, the bands may stretch down into the red. With an exposure of 1½ minutes there is barely an indication of bands, and when the quantity of the chloride is reduced to 0·025 gramme, there is nothing but a continuous spectrum to be seen. Potassium cyanide and ferrocyanide with the same exposure both yielded very dense spectra, but on that account the bands are not seen distinctly. They are well seen in spectra photographed from potash alum, potassium carbonate, and potassium ferricyanide. Between the wave-lengths of two cadmium lines, 4800·8 and 4414·5, ten of these bands were counted. They are not sharp at the edges, and the spaces between successive bands decrease as they tend towards the violet. They appear, in fact, like a continuation of the subordinate series of lines, 4808·8, 4803·8, 4796·8, 4788·8, and 4759·8 (Liveing and Dewar), but they are diffuse. There is an absence of any accompanying fine lines such as are seen in the lithium and sodium spectra. Spectra from sodium and potassium carbonates have recently been photographed with Wratten and Wainwright's panchromatic spectrum plates, which give the lines well defined with the continuous rays from wave-lengths 7699·3 and 7665·6 of potassium to a line 3303·1 which belongs to sodium. There is a strong band in the red, extending from $\lambda 6911$ to $\lambda 7350$, fading away rather abruptly on the less refrangible side,

but with feeble continuous rays extending to λ 7665·6. The bands mentioned above are seen to be composed of two groups; the one nearer the red appears like the continuation of the subordinate series of lines with the spaces between them decreasing, and the second group more towards the violet, where the bands do not appreciably vary in width or in distance apart.

Rubidium Salts.—Sulphate and chloride of great purity yielded merely a continuous spectrum in which there are no bands, but the lines are very broad and strong.

Cæsium Salts.—The same effect is seen with the corresponding salts of cæsium.

Banded Spectra from the Alkaline Earth Salts.

The banded spectra observed with barium chloride and strontium sulphate are reproduced, but with a dispersion of only one prism on Plate 6, in " Flame Spectra at High Temperatures."[*] In course of a study of the oxyhydrogen flame spectra of calcium, strontium, and barium compounds, made in 1902, bands were constantly observed in minerals containing barium, just as the bands of lead are constantly seen in the flame spectra of minerals containing lead and, subsequently, the barium bands were photographed from the flame spectra of very carefully prepared compounds which were spectroscopically pure.

The bands in the continuous background of rays are different from those of the alkali metal group. In calcium and strontium the most conspicuous bands are broad and disposed somewhat irregularly, but in detail the spectra of calcium, strontium, and barium compounds show bands of two varieties, the one broad overlying narrow bands; when the quantity of material is small, only the narrow bands are seen, and when the slit is not narrow enough they appear as diffused rays or a continuous spectrum. As in the lithium, sodium, potassium group, the calcium, strontium, and barium spectra differ much in intensity, and follow in the same order as the alkali metals in this respect, which is that of the numerical values of the atomic weights of the metals, the higher the value the greater the volatility of the compound. The strontium and barium chlorides exhibit the banded spectra best, but they are well seen also in sulphates, carbonates, and oxides. The best mineral in which to study the bands of calcium is the natural sulphate, selenite. It should not be overlooked that compounds yield their own spectra, such as chlorides, under certain conditions, phosphates and fluorides, as, for instance, ferrous phosphate and calcium fluoride. The oxides B_2O_3 and P_4O_{10} also emit their own spectra, but

* ' Phil. Trans.,' 1894.

whereas the former shows bands, the latter shows lines only. This has been made the basis of a method of separating alkali metal flame spectra from those of the alkaline earth metals.* Bands characteristic probably of the sulphates may be found to overlie the metal bands.

Several different compounds of barium have all been found to yield the same banded flame spectrum when a sufficient quantity of substance is introduced into the flame, and all strontium salts also yield in like circumstances the same flame spectrum. When the sulphates of the alkaline earths are submitted to the oxyhydrogen flame, they all yield the banded spectra, and in the case of calcium and strontium sulphates, also certain lines in addition, but barium sulphate frequently shows only the bands without the barium line; therefore, the lines appear more readily than the bands with calcium salts, and the bands more readily than the lines with barium compounds. In fact, barium behaves in this respect very much as lead does.

There is an important difference in the chemical nature of the three sulphates after being heated in the flame: thus, the barium sulphate is entirely reduced to sulphide, so that we arrive at the fact that the same spectrum is common to chloride, oxide, and sulphide. But the chlorides are converted by the water-vapour in such a flame into oxides, so that we have simply the oxide and sulphide to consider.

The strontium sulphate is reduced partly to oxide and partly to sulphide under precisely the same conditions, and the calcium salt is simply converted into oxides. As the oxide produced from the chloride and sulphide produced from the sulphate of barium yield exactly the same banded spectrum, it is evident that we are dealing with the spectrum of the only constituent in common, which is the metal. It is quite inconceivable that the oxide and sulphide should give identical spectra of the respective compounds because the molecular weights of the compounds are different. The same observation applies to the compounds of strontium, which yield spectra with lines and bands, but we know that strontium sulphate, after it has been removed from the flame, has by less than one-half been reduced to sulphide; it is, therefore, probable that in this case as in that of barium, the spectrum is caused either by the dissociation of the sulphide in the flame or by a chemical reduction. Calcium sulphate is not simply deoxidised in the flame, like the corresponding salts of strontium and barium, but is converted into lime, yet this compound exhibits both lines and bands.

* ‘Chem. Soc. Trans.,’ 1893, vol. 63, p. 138.

Evidence of Thermo-chemical Reduction of Refractory Oxides in the Flame.

It has already been shown that aluminium can be reduced from its oxide in the oxyhydrogen flame, that it colours the flame and emits the two lines $\lambda\lambda$ 3967 and 3946. It was concluded that bands which have been attributed to the oxide are in reality metal bands.[*] Bands of beryllium and lanthanum were also reduced from their oxides; the greater volatility of metallic beryllium[†] caused the band spectrum to be photographed without the lines.

I have now arrived at the conviction, from additional evidence presently to be adduced, that calcium and strontium are also produced in the oxyhydrogen flame by thermo-chemical reduction of their oxides and sulphides.

The question of the reduction of the oxides of the dyad and triad groups is quite different from that of the oxides of the alkali metals, because compounds of the latter are not only easily volatilised, but it has been proved by St. Claire Deville that in the manufacture of the alkali metals, the oxides are thermo-chemically dissociated, and then reduced by carbon entering into immediate combination with the dissociated oxygen.

Spectro-chemical Evidence from Anhydrous Flames and Dehydrated Salts.

By an anhydrous flame is meant one in which water is not a product of combustion. Any salt which yields the spectrum, or imparts the character-istic colour of the metal to such a flame, is excluded from the view of Arrhenius that vapourised salts are first hydrolysed by water-vapour in the flame, that the hydroxides thus formed undergo ionisation, and the spectra are caused by the metallic cations. Smithells, Dawson, and Wilson first applied this test to alkali salts, by heating them in the flame of burning cyanogen.[‡] Lenard also has observed that sodium salts colour the flame of carbon disulphide. The authors aforesaid suggest that a chemical reduction takes place and the metal then colours the flame. I have extended this enquiry by placing anhydrous salts in the flame of carbon monoxide. Smithells has shown that, if this gas be carefully dried, it will not inflame when issuing from a jet, but if the jet be heated the gas ignites. It has also been shown[§] that carbon monoxide stored over water in a gasholder will not inflame in air if the jet be small like that of a Bunsen or ordinary "bat's wing" burner, but it will burn from a tube if the orifice be wide enough,

[*] 'Banded Flame Spectra of Metals,' p. 346, and Plate XXXI.

[†] This was observed by Pollok in its reduction by the arc.

[‡] 'Roy. Soc. Proc.,' 1899, vol. 64, p. 142.

[§] Hartley, "On the Temperature of Certain Flames," 'Chem. Soc. Trans.,' 1896, vol. 69, p. 844.

and even from a "bat's wing" burner when the pressure is small; though in these latter circumstances the flame is very small. In view of these facts, pure carbon monoxide was most carefully dried, first with a column of pumice saturated with oil of vitriol, and then with two large tubes of phosphoric anhydride.

The gas was conducted into a platinum tube with an internal diameter of 6 mm. and a length of 30 cm. It was found that under these conditions the gas was very difficult to inflame, but it did burn; nevertheless, to increase the temperature and render the same steady by ensuring combustion, the tube was heated red-hot by a Mecke burner placed 3 inches from its orifice.

On introducing into the flame recently ignited carbonates of lithium, sodium, and potassium, even without heating the platinum tube, beautiful spectra were observed, such as are visible in the flame of a Bunsen burner. It was very difficult to see the red line of potassium about λ 7660, but the green glow and a group of green lines about λ 5800 were observed. Experiments were tried in both the inner and outer cones, but only when the substance was heated at the tip of the inner cone could the group of green lines be seen. In this instance it is not reasonable to suppose that sufficient water could gain access to the flame to give rise to hydrolysis, and, in fact, hydrolysis could not take place.

The same experiments were repeated with the oxides, carbonates, nitrates of calcium, strontium, and barium; but although the platinum tube was heated to bright redness, there was no trace of a spectrum of either bands or lines in any case. Calcium, strontium, and barium chlorides, on the other hand, showed superb spectra of the chlorides, apparently identical with those produced by heating the same salts in a coal-gas flame saturated with hydrochloric acid. The temperature of this carbon-monoxide flame, which was from 50 to 75 mm. long, is higher than that of a Bunsen burner of the same size,* and can raise a larger mass of material to a higher temperature.† Here we have evidence that the metals of the alkalies behave quite differently from those of the alkaline earths; calcium, strontium, and barium chlorides are volatile without decomposition, for they fuse and remain clear liquids without showing turbidity for as long as is necessary to observe their spectra. Inasmuch as they appear to yield their own spectra, they behave like calcium fluoride when placed in the oxyhydrogen blow-pipe flame, and doubtless other similar fluorides and phosphates. The most important facts ascertained so far are, first, the alkaline earth oxides are not

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* *Loc. cit.*

† Platinum wire 1/40th mm. in thickness can be melted into a globule in any part of the flame.

volatile in the carbon-monoxide flame, or, if they are, they show no spectrum; second, the flame is a powerful reducing one to all oxides with a heat of formation not greater than that of zinc oxide, but the oxides in question are not reduced; thirdly, the temperature of the flame is higher than that of a Bunsen burner, and over a large area it is nearly as high as that of the oxyhydrogen flame; fourthly, the chlorides are volatile in an anhydrous flame, but the stability of the chlorides in such a flame is somewhat doubtful, as they may undergo dissociation.

The action of the cyanogen flame is very different from that of the flame of carbon monoxide, because cyanogen is a very powerful reducing agent.

When calcium oxide was introduced on a platinum wire into the flame of cyanogen burning in air, there was no action low down in the flame, but when the substance was placed at the tip of the inner cone, there was a magnificent display of the same spectrum as that seen when calcium metal is burnt in air, and with no trace of the cyanogen bands. The effect on baryta was tested in a similar manner, by making pure barium carbonate into a stiff paste with water, and moulding it round a loop of platinum wire. On placing this in the flame at the same point, an equally fine spectrum of barium was obtained. In both instances the spectra were identical with those photographed when the same compounds were placed in a Mecke burner, but the brilliancy and intensity of the rays were greatly increased.

Beyond all doubt these spectra are the spectra of the metals.

The deductions from these facts are, that the lines and bands seen in the oxyhydrogen flame are certainly not the spectra of the oxides, because if the difference between this and the carbon monoxide flame were simply one of temperature, the emission spectra of oxides and sulphides should be quite as easily produced in a carbon monoxide flame as in one of hydrogen. Finally, carbon monoxide was burnt with oxygen in a Deville blow-pipe and still no spectrum of calcium or strontium was seen, except when traces of chloride were present. The salts were supported on very thin slips of Donegal kyanite.

The presence of hydrogen in the flame is, therefore, a necessary element in some chemical reaction which leads to the reduction of the sulphides or oxides to the metallic state. The temperature of these flames, which can melt platinum, is sufficient to effect the thermo-chemical dissociation of water-vapour, and it is probable that in this lies the cause of the spectra appearing.

Spectra of the metals observed in a carbon monoxide flame on the grandest scale are those which were photographed from the Bessemer "blow," but in this case the spectra are not due to the heating of a substance in a pure gas

or even in a mixture of gases, but are the result of the internal combustion of impurities in the metal, which causes the vapours to be carried off in a stream of intensely heated carbon monoxide mixed with nitrogen and a small proportion of hydrogen, all of which gases, except the nitrogen, are burnt in the air. The average vapour pressure of water in the blast amounts to about 1 *per cent.* of the air; this is reduced by the metal bath to hydrogen and carbon monoxide and, as the temperature is an exceedingly high one, it is not surprising that a line spectrum of calcium seen in the oxyhydrogen flame has been photographed in the Bessemer flame, the flame being a mixed hydrogen and carbon monoxide one. The lines are, however, only two, namely, 4226·9 and 4581·6. Arguments from Bessemer flame observations rather lead to confusion, on account of the many other elements present in the flame, and they must therefore be rejected or treated with discrimination.

It will be observed that in the groups Li, Na, K, and Ca, Sr, Ba, the facility with which the bands are produced increases with the atomic weights, likewise the volatility of metals increases in the same order, and as, in the first group, the elements are monatomic, the relative vapour densities are half their atomic weights; accordingly we have 7/2, 23/2, 39/2 as the relative quantities of matter in the flame if they have all the same volatility and if their oxides undergo dissociation with equal facility; but the least easily dissociated is the least volatile lithium oxide; we may therefore say that the vapour pressure of potassium will be at least six times that of lithium in any flame in which the two oxides are placed under the same conditions. As there is very little difference between the heats of formation of the groups of oxides, CaO, SrO, and BaO, the energy required for their reduction may be considered to be the same for each oxide. The respective volatilities of the oxides or of the metals is not known, neither are we acquainted with their vapour densities; accordingly we may assume them to be either monatomic or diatomic molecules; if the latter, then the relative quantities of vapour in the flame will be in the proportion of the atomic weights, or 40, 87·6, and 137·4; if they are monatomic, half these quantities, which gives three and a-half times as much vapour of barium in the flame as of calcium, under the same conditions in either case. If, however, we attempt to compare the vapour densities of the alkali metals with those of the dyad group as judged by their spectra, we are at once met with a difficulty by the reactions in the flame by which the metals are set free, being different for each group.

Part II.—On the Chemical Reduction of the Alkaline Earth
Sulphates.

For studying the action of gases in the flame on the insoluble sulphates, the minerals heavy spar, celestine, and selenite were chosen. Pieces of each measuring about 15 × 15 × 2 mm. were held by platinum forceps in the oxyhydrogen flame for a definite period, and then dropped into a measured volume (50 c.c.) of water. The unaltered mineral was insoluble in each case, but that which had undergone reduction, whether to oxide or sulphide, dissolved with a strongly alkaline reaction ; the metal in solution was therefore determined volumetrically with standard acid. From the dissolved salts obtained from heavy spar, sulphuretted hydrogen was evolved in large quantity, somewhat less in the case of celestine, and hardly a trace with selenite. The following tabulated statement shows the results obtained :—

	Anhydrous salt.		
	$CaSO_4$.	$SrSO_4$.	$BaSO_4$.
Time in flame	15 mins.	15 mins.	10 mins. 15 mins.
Metal in solution ...	0·0436 grm.	0·1150 grm.	0·1055 grm. 0·1820 grm.
Metal as sulphide ...	Practically none	10 per cent.	Practically all.

If numbers be taken proportional to the above quantities, they are found to be approximately in the ratio of the atomic weights of the elements, thus :—

$$0·0436 \text{ gramme} : 0·115 \text{ gramme} : 0·182 \text{ gramme} = 34 : 88 : 139$$
$$Ca \quad : \quad Sr \quad : \quad Ba \quad = 40 : 87·5 : 137$$

A sample of celestine was heated in the flame for 35 minutes and dropped into water, acidified with acetic acid, and the sulphuretted hydrogen precipitated as lead sulphide which was filtered off, converted into lead sulphate and weighed. The excess of lead was removed and the excess of strontium determined as carbonate.

Weight of lead sulphate ...... 0·0314 gramme.
Strontium as SrS .... 0·0091   „
Strontium carbonate .... 0·1718   „
Strontium as SrO .... 0·1022   „

These figures show that 8·1 per cent. of the strontium in solution is in the state of sulphide.

The quantity of strontium reduced from sulphate in 35 minutes was 0·1022 gramme, whereas that reduced in 15 minutes was 0·115 gramme, or the longer period in the flame has yielded the smaller product.

The Reduction of Barium Sulphate to Sulphide by Hydrogen.

A current of dry hydrogen was passed over a weighed quantity of precipitated dried barium sulphate, heated to redness in a platinum tube. It was soon observed that sulphuretted hydrogen was evolved, probably according to the equations following :—

$$(1) \quad BaSO_4 + 4H_2 = BaS + 4H_2O.$$
$$(2) \quad BaS + H_2O = BaO + H_2S.$$
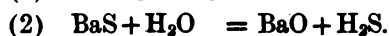
Sulphuretted hydrogen was still being evolved after a period of eight hours, when the experiment was stopped.

$BaSO_4$, initial weight............	0·3226 gramme	= Ba 0·1897 gramme.
$BaSO_4$, residue unchanged ...	0·0059 „	= Ba 0·0035 „
Difference, substance reduced	0·3167 „	= Ba 0·1862 „
$PbSO_4$ from BaS, found	0·2822 „	
Ba in BaS, found	0·1276 „	
Ba in BaO, found	0·0586 „	
Total Ba in $BaSO_4$ reduced ...	0·1862 „	

The reduced $BaSO_4$ is thus seen to have been composed of BaS = 0·1574 gramme, and BaO = 0·0654 gramme ; or about two-thirds sulphide and one-third oxide.

There can be no doubt that the initial action of the hydrogen is the reduction of the sulphate to sulphide, and that probably the whole of the sulphate is reduced; the secondary action, whereby the sulphide is converted into oxide with evolution of sulphuretted hydrogen, is slow and gradual with the barium compound, but takes place with greater facility with strontium, and with completeness in the case of calcium.

When heated to bright redness in a platinum tube through which a current of nitrogen and of carbon dioxide is passed, barium sulphate in neither instance undergoes any change.

When submitted to a white heat in a platinum tube at a reduced pressure for 15 minutes, barium sulphate evolved no oxygen and the substance showed no alkalinity and was quite unchanged.

These experiments show that the hydrogen of the flame is the reducing agent by which the spectra are produced.

Part III.—The Thermo-chemistry of the Reduction Processes in Flame Reactions.

In studying the thermo-chemistry of flames, it is necessary to consider three separate questions:—

(1) The effect on compounds of high temperatures solely.

(2) The chemical action of other reacting substances in the flame gases on the compound in the flame.

(3) The combined effect of high temperatures and reducing gases. .

The thermo-chemical notation used is that of Dr. James H. Pollok.[*] The solid, liquid, gaseous, and dissolved states are indicated where necessary by a dot, dash, T, or circle (• — T O), placed below the formula of the substance. The heat evolved in the formation of a compound is indicated by ξ placed before its formula, which signifies *energy*.

The heat of a reaction is indicated by enclosing the equation in brackets and placing ξ before it. K° signifies a kilogramme degree of heat, or large calorie, k° similarly is a gramme degree of heat, or small calorie.[†] The chemical formula for a substance means, as is usual in this connection, its gramme-molecular weight.

In discussing the process of hydrolysis of alkaline chlorides in the flame, we must take into account the following values and place the reaction at a temperature approaching 2000°, then

$$\xi\text{HCl} = 26 \text{ K}° \quad \text{and} \quad \xi\text{H}_2\text{O} = 50\cdot6 \text{ K}°.$$

The heat of formation of solid potassium and sodium hydroxides is thus represented—

$$\xi(\text{K}+\text{H}+\text{O} = \text{KOH}) = 104\cdot6 \text{ K}°;$$

similarly, $\xi\text{NaOH} = 102\cdot7 \text{ K}°.$

The hydrolysis is then

$$\xi(\text{KCl}+\text{H}_2\text{O} = \text{KOH}+\text{HCl}) = -25\cdot7 \text{ K}°.$$
$$\quad\;\;105\cdot7 \quad 50\cdot6 \quad\;\; 104\cdot6 \quad 26$$

The corresponding value for NaOH is $-19\cdot8$ K°.

These reactions are not very strongly endothermic and therefore may occur, and are reversible.

Among the common salts of lithium the sulphate has the greatest stability, nevertheless in a gas flame it is reduced to oxide. Fused lithium sulphate was found to be a perfectly neutral substance, but when a bead of the salt had been heated in the flame of a Mecke burner for an hour it yielded a strongly alkaline solution which did not evolve sulphuretted hydrogen when acidified, nor did it effervesce. It therefore contained the oxide. On taking a larger mass and heating it on kyanite in the oxy-coal-gas blow-pipe flame, care being taken that there should be no free carbon, the

* 'Sci. Proc. Roy. Dublin Society,' 1899, and 'Chem. Soc. Trans.,' 1904, vol. 85, p. 603.

† For the convenient symbol g° C., or gramme degrees Celsius, instead of heats units, or calories, and kilogramme degrees of heat, K° C., we are indebted to Mr. J. Y. Buchanan, "On Steam and Brines," 'Trans. Roy. Soc. Edin.,' 1894, vol. 39, Part III, pp. 529—573.

fused salt became reduced to sulphide. From this it appears that the normal process of reduction of the sulphates in the flame is that given in the two equations referring more particularly to barium sulphate. The difference in the heat of formation of lithium oxide and sulphide respectively, $\xi \text{Li}_2\text{S} = 115\cdot4 \text{ K}^\circ$ and $\xi \text{Li}_2\text{O} = 141\cdot2 \text{ K}^\circ$; this shows how readily the former may be converted into the latter by the action of water-vapour, $\xi \text{H}_2\text{O} = 69 \text{ K}^\circ$, by reason of its being an exothermic action.

The flames from coal-gas, hydrogen, and carbon monoxide respectively, when burning in air, have a temperature as high as that of the melting point of platinum, 1775° C. This temperature exceeds that of the metallurgical furnaces, in which sodium, potassium, cadmium, zinc, and magnesium are reduced and distilled on an industrial scale.

In the manufacture of sodium and potassium from the respective carbonates by means of carbon, the oxide is vapourised and chemically dissociated, thus $\text{Na}_2\text{O} = 2\text{Na} + \text{O}$, but the action is not reversible, owing to the presence of carbon, which immediately forms carbon monoxide with the oxygen, thus—

$$\xi(\text{C}+\text{O} = \text{CO}) = 29\cdot4 \text{ K}^\circ \quad \text{and} \quad \xi(\text{CO}+\text{O} = \text{CO}_2) = 68\cdot3 \text{ K}^\circ;$$

therefore, on the whole we have

$$\xi \text{CO}_2 = 97\cdot4 \text{ K}^\circ.$$

But $\quad\quad\quad \xi \text{Na}_2\text{O} = 100\cdot2 \text{ K}^\circ \quad \text{and} \quad \xi \text{K}_2\text{O} = 98\cdot2 \text{ K}^\circ,$

so that where the carbon is oxidised to carbon monoxide only, we have a considerable endothermic action, thus—

$$\xi(\text{Na}_2\text{O} + \text{C} = \text{CO} + 2\text{Na}) = -71\cdot4 \text{ K}^\circ, \text{ endothermic.}$$

Although this equation does not take into account the fact that the Na_2O is already dissociated, this endothermic action may easily tend towards an exothermic character by the further combustion of the carbon monoxide to carbon dioxide, thus—

$$\xi(2\text{Na}_2\text{O} + \text{C} = 4\text{Na} + \text{CO}_2) = -102\cdot8 \text{ K}^\circ,$$

$$\underset{200\cdot4}{} \quad\quad\quad \underset{97\cdot6}{} \quad \underset{\text{Endothermic}}{}$$

or for one atom of oxygen $\quad\quad -51\cdot4 \text{ K}^\circ.$

If we suppose the operation to be a simple one of reduction, we have—

$$(\text{Na}_2\text{CO}_3 + 2\text{C} = 2\text{Na} + 3\text{CO}) = -82\cdot6 \text{ K}^\circ.$$

$$\underset{270\cdot8}{} \quad\quad\quad\quad \underset{29\cdot4 \times 3}{}$$

The reduction of K_2CO_3 in like manner would result in an endothermic value of $-90\cdot6 \text{ K}^\circ$. The same reasoning does not apply to lithium oxide, for all attempts to obtain lithium by a similar process of reduction have entirely failed. The reason is, that lithia more nearly resembles the alkaline earth oxides in its chemical properties; it is also the least volatile and least fusible

of the alkali group; moreover, the energy required for its reduction is greater than that necessary for potassium or sodium. Thus

$$\xi\text{Li}_2\text{O} = 141\cdot2\ \text{K}^\circ \quad \text{and} \quad \xi\text{Na}_2\text{O} = 100\cdot9\ \text{K}^\circ.$$

An important fact may be observed here, namely, that whereas the banded spectrum of potassium is comparatively easy to obtain, that of lithium is very difficult, more difficult than that of sodium, and even the continuous rays are very weak. The same must be said of rubidium, with the additional remark that its band spectrum has never yet been seen.* This, undoubtedly, in part arises from the high value for the heat of formation of the oxides of these metals, and it is obvious that these particular properties of lithium serve to explain why the continuous glow observed by Lenard in the case of lithium is weaker than that of either sodium or potassium, which led him to remark that it was probably a property peculiar to that element. Even rubidium carbonate was reduced by mixing with carbon and heating to a particularly high temperature (Bunsen), but the greater volatility of rubidium compounds may facilitate their dissociation.

It is quite evident, then, that with the fusible and volatile oxides of sodium, potassium, and rubidium, reduction can be effected at a temperature not exceeding a white heat and probably about 1400° C., certainly below the temperature of melting platinum, and below the highest temperatures of the coal-gas, the hydrogen, and the carbonic oxide flames.

Hence I conclude that the banded spectra of lithium, sodium, and potassium observed at the temperature of the oxyhydrogen flame are the spectra of the metals.

The Alkaline Earths.

It has been shown that these substances are of a different nature and their salts are sharply divided into two classes, the haloid and the oxy-salts, each with a different behaviour.

The Haloid Salts.—These are volatile in flames supplied with the halogen hydrides without decomposition. They are also volatile without decomposition in a dry carbonic oxide flame. Here, then, we may probably have the spectra of salts and not of the metals. In a hydrogen or coal-gas flame the salts are hydrolysed and converted into oxides by heat; this is a fact well known. If we examine the heat of formation of the chlorides, we find it to be, for calcium and strontium respectively,

$$\xi\text{CaCl}_2 = 169\cdot9\ \text{K}^\circ \quad \text{and} \quad \xi\text{SrCl}_2 = 184\cdot7\ \text{K}^\circ,$$

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* A note appears on one of my photographs that there are just faint indications of bands in the strong continuous spectrum.

while the oxides are

$$\xi CaO = 131\cdot5 \text{ K}° \quad \text{and} \quad \xi SrO = 131\cdot2 \text{ K}°.$$

The barium chloride has not been determined, but the oxide is

$$\xi BaO = 133\cdot4 \text{ K}°,[*]$$

and we may therefore safely say that the energy of formation of the chloride does not differ much from the number deduced from strontium chloride or about 187 K°.

The effect of water-vapour in the flame is an endothermic reaction when the chloride is a solid.

$$\xi(CaCl_2 + H_2O = CaO + 2HCl) = -37\cdot5 \text{ K}° ;$$
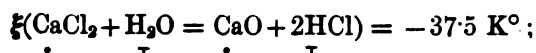
and where towards 2000° C.,

$$\xi H_2O = 50\cdot6 \text{ K}° \quad \text{and} \quad \xi CaO = 131\cdot5 \text{ K}°.$$

The corresponding value for $SrCl_2$ is $-52\cdot1$ K°. When the chlorides are vapourised in the flame, these endothermic values must be much less and the reactions are easily reversed, as we know by experience when gaseous hydrochloric acid or much ammonium chloride is passed into the flame. We can see clearly also why it is that the carbonic oxide flame does not decompose these salts, the heat of combination of the chlorides being much in excess of that of the oxides, and the reducing power of carbonic oxide, which is the converse of the energy of formation of carbon dioxide, much less, thus :—

$$\xi(CO + O = CO_2) = 68\cdot3 \text{ K}°.$$

It is different with cupric chloride, as this in time is reduced to copper.

The Oxy-salts.—These are all resolved into either oxides or sulphides, or mixtures of the two, when heated in the oxyhydrogen flame. The energy of formation of the oxides is as follows :—

$$\xi CaO = 131\cdot5 \text{ K}°, \quad \xi SnO = 131\cdot2 \text{ K}°, \quad \text{and} \quad \xi BaO = 133\cdot4 \text{ K}°,$$

there being very little difference between them, but these values are all below those of lithium and rubidium, where

$$\xi Li_2O = 141\cdot2 \text{ K}° \quad \text{and} \quad \xi Rb_2O = 165\cdot4 \text{ K}°.$$

We have now to take into consideration the reducing power of hydrogen at high temperatures in flame reactions. There are two values for the production of gaseous water, the smaller of which is at a temperature approaching 2000°, which we may consider to be the highest temperature of all flames capable of melting platinum—

$$\xi H_2O = 58\cdot1 \text{ K}° \quad \text{and} \quad \xi H_2O = 50\cdot6 \text{ K}°.$$

[*] A. Guntz, 'Comptes Rendus,' 1903, vol. 136, p. 1071.

The decreasing value at high temperatures is evidence of the dissociation of water-vapour, which we know does occur at the temperature of white hot platinum. Now both the above values are below that obtained by the combustion of carbon monoxide.

$$\xi(\underset{\tau}{CO} + \underset{\tau}{O} = \underset{\tau}{CO_2}) = 68 \cdot 2 \; K^\circ;$$

it is, therefore, unnecessary to consider a coal-gas flame apart from one fed with hydrogen, for many of the reductions and dissociation phenomena that can take place in the latter may occur in the former.

The high temperature tends to the dissociation of other oxides than water, and the alkaline earths are most certainly volatilised in Deville's blow-pipe flame, whether they are first dissociated or not. Furthermore, reduction processes are carried on in the solid material, which have not hitherto been suspected, such as the reduction of strontium and barium sulphates to sulphides and of beryllia and alumina to the state of metal.

In the metallurgical process of zinc distillation, the presence of carbon mixed with the ore is necessary. The energy of formation of zinc oxide is $\xi ZnO = 84 \cdot 8 \; K^\circ$. Supposing the reduction to take place through the medium of carbon monoxide, we have the following:—

I. $\xi(ZnO + C \quad = Zn + CO) \quad = -55 \cdot 4 \; K^\circ.$
II. $\xi(ZnO + CO = Zn + CO_2) = -16 \cdot 5 \; K^\circ.$
    $\quad 84 \cdot 8 \qquad\qquad\qquad 68 \cdot 3 \quad \text{Endothermic.}$
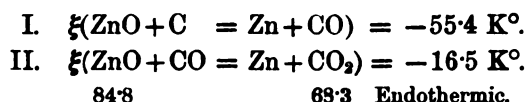
In this case we are considering a solid oxide, not one in the state of vapour; nevertheless we know that reduction does occur though the reaction is endothermic. By recent observations it has been shown that zinc oxide is vapourised at 1400° and rapidly at 1700° C.[*] and this must greatly facilitate the reduction process.

The reduction of cadmium is more easily accomplished than that of zinc, and hence the cadmium distils over first. The obvious reason for this is that the heat of formation of the oxide is about 21 K° less than that of zinc oxide and $\xi CdO = 65 \; K^\circ$; we have, then, the following equation:—

$$\xi(CdO + C = Cd + CO) = 3 \cdot 2 \; K^\circ.$$

The reduction of cadmium is a feebly exothermic process. Let us take another instance, that of the reduction of a solid oxide such as alumina.

The combination of this with oxygen gives an amount of energy which has not hitherto been measured directly, but the heat of formation of the colloidal hydroxide is known, and it must be accepted as being somewhat

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[*] F. O. Doltz and C. A. Grammann, 'Metallurgie,' 1906, vol. 3, p. 212, also pp. 372—375.

greater than that of the oxide, but only slightly greater. It is expressed by the following equation:—

$$\xi(2Al + 3O + xH_2O = Al_2O_3 \cdot xH_2O) = 393 \text{ K}^\circ.$$

All attempts to reduce alumina by means of carbon alone, or carbon acting jointly with carbon monoxide on an industrial scale have failed, though many such processes have been devised.

The fact may be accounted for by the following equations:—

$$\xi Al_2O_3 = 393 \text{ K}^\circ \quad \text{or} \quad \xi\tfrac{1}{3}Al_2O_3 = 131 \text{ K}^\circ \text{ endothermic};$$

$$\xi(2Al_2O_3 + 3C = 4Al + 3CO_2) = -495 \text{ K}^\circ.$$
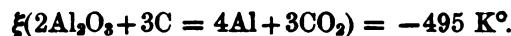
or, for 1 atom of oxygen removed, -82.5 K$^\circ$.

Substituting for solid carbon, gaseous hydrogen, we have

$$\xi(\tfrac{1}{3}Al_2O_3 + H_2 = \tfrac{2}{3}Al_2 + H_2O) = -72.9 \text{ K}^\circ,$$

not a very great difference. Substituting gaseous carbon monoxide for solid carbon, we obtain

$$\underset{393}{\xi}(Al_2O_3 + 3CO = 2Al + \underset{68.3 \times 3}{3CO_2}) = -188.1 \text{ K}^\circ,$$
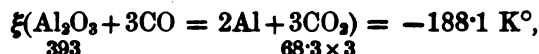
or, for 1 atom of oxygen removed, $\tfrac{1}{3}$ of this $= -62.7$ K$^\circ$.

The actual energy supplied in these reactions before the aluminium can be reduced is for carbon, carbon monoxide, and for hydrogen respectively, -82.5 K$^\circ$, -62.7 K$^\circ$, and -72.9 K$^\circ$. The carbon monoxide value is thus shown to be less than that in either of the other two reactions. It has already been proved, first, that alumina is reduced to the metallic state in the oxyhydrogen flame; secondly, that the reduction takes place more easily when the alumina is mixed with some dense form of carbon. In the first instance, the flame alone supplied hydrogen only as the reducing agent, consequently, the energy required for every atom of oxygen removed was 72.9 K$^\circ$ in the form of extraneous heat which was necessary not only for initiating the process, but also maintaining it. When solid carbon was used, this was a somewhat higher figure, being 82.5 K$^\circ$, but this very reduction process with solid carbon would result in the formation of carbon monoxide which could then operate upon another molecule of alumina, which places the extreme limits of the energy required for reduction as between 63 K$^\circ$ and 82.5 K$^\circ$. From this it would appear that *any reducing process may be carried out in the oxyhydrogen flame by a purely chemical action if the extraneous energy required to initiate and maintain the action does not exceed** 84.8 *K$^\circ$ per atom of oxygen to be removed.*

* This is the figure for the zinc reduction $\xi ZnO = 84.8$ K$^\circ$, that calculated for alumina is 82.5 K$^\circ$.

Let us now consider another instance of the reduction of a solid oxide in the flame, namely, beryllia. The energy of formation of the oxide is unknown, but its composition is BeO.

Pollok has measured the heat of formation of the chloride $\xi BeCl_2 = 155$ K°, and of the heat of dissolution of beryllium in aqueous hydrochloric acid $\xi BeCl_2 = 199\cdot5$ K°. Comparing these results with the heat of formation and solution of aluminium chloride, we obtain the following figures:—

	Al_2Cl_6.	$\frac{1}{3}Al_2Cl_6$.	BeCl
Heat of formation	323·6	107·9	155·0
Heat of solution............	152·6	50·9	44·5

Similar comparisons, made with magnesium and zinc chlorides, give

	$BeCl_2$.	$MgCl_2$.	$ZnCl_2$.
Heat of formation	155·0	151·0	97·4
Heat of solution............	44·5	36·0	15·6

These figures show that in each case a fall in the heat of formation and solution accompanies the rise in the atomic weights.

Now $\xi Al_2O_3 = 393$ K° $= \xi\frac{1}{3}Al_2O_3 = 131$ K°,

and $\xi\frac{1}{3}Al_2Cl_3 = 107\cdot9$ K°,

the difference, 23·1 K°, shows that the energy of formation of the oxide is by that amount greater than the chloride, and as

$$\xi BeCl_2 = 155 \text{ K°,}$$

we may assume the value

$$\xi BeO = 178\cdot1 \text{ K°}$$

to be approximately correct. But

$$\xi MgO = 143\cdot4 \text{ K°} \quad \text{and} \quad \xi ZnO = 84\cdot8 \text{ K°,}$$

also $\xi MgCl_2 = 151\cdot0$ K° $\quad$ and $\quad \xi ZnCl_2 = 97\cdot4$ K°,

the difference between magnesium chloride and oxide is 7·6 K° and between zinc chloride and oxide 2·6 K°, we may assume then that $\xi BeO = 148$ K°, and this number is very probably more correct than that derived from the figures obtained from a comparison of the difference between the oxide and chloride of aluminium, because magnesium and zinc belong to the same group as beryllium, and aluminium does not.

The metal is certainly reduced from the oxide by the oxyhydrogen flame, and, as far as we know, beryllia is not a volatile oxide, nor is it fusible. The reduction must, therefore, be the result of a purely chemical action, and it must also be of a highly endothermic character, as may be seen by the equation following:—

$$\xi(BeO + H_2 = Be + H_2O) = -97\cdot4 \text{ K°.}$$
$$148 50\cdot6 \quad \text{Endothermic.}$$
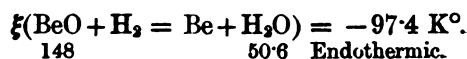
It may be inferred from the evidence afforded by the flame spectra, that at these high temperatures the infusible and non-volatile metallic oxides are in a peculiarly active condition, having absorbed a large amount of energy from the flame, so that they are approaching the condition of dissociation and are, therefore, subject to chemical interactions with the reducing gases, which otherwise would have no power to reduce them. But in the cases referred to, the reducing gas is hydrogen, and in all probability it is not the hydrogen supplied to the flame in the molecular condition, but hydrogen in the atomic or nascent state, resulting perhaps from the dissociation of water, the product of combustion in another part of the flame, which carries with it the additional charge of energy which enables it to initiate and complete the reduction process.

Conclusions.

(1) The oxides of calcium, strontium, and barium, are not dissociated by heat alone, because they show no spectrum in a carbon monoxide flame ; (2) They are reduced by the combined action of heat and hydrogen in the oxy-hydrogen flame and by the action of cyanogen in the cyanogen flame ; (3) The flame coloration is due to the metal, because not only is the flame spectrum from lime essentially the same as that of the metal calcium, but also the heats of formation of CaO, SrO, and BaO have very nearly the same value, and that where calcium oxide can be reduced the other oxides could, on that account, undergo a similar reduction. Whether the compound of strontium or barium in the flame be a sulphide or an oxide, the same spectrum is emitted, but there is some uncertainty as to whether the barium sulphide is not converted into oxide by water-vapour in the flame.

The explanation given by Lenard, of the flame coloration by the alkali salts, appears to be inapplicable to the coloration of the carbon monoxide flame by the haloid salts of the alkaline earth metals.

On the Resistance of Air.

By A. MALLOCK, F.R.S.

The great mass of work, both theoretical and experimental, which has been done on this subject may be divided into two classes, one of which comprises all the results having reference to such moderate velocities as can be obtained with artificially produced currents (*i.e.*, up to about 100 f.s.), while the other is confined to velocities about and exceeding the velocity of sound. Between these two there is a gap in the experimental record extending over a range of nearly 1000 f.s.

I am not aware that any attempt has been made to connect theoretically the experimental results at high and low velocities, and it is the object of this paper to find an expression which will represent the resistance generally.

The expression which is arrived at does not pretend to be anything but an arbitrary formula, but it is, I think, useful as separating the resistance into its component parts, and also as indicating the class of experiment which is needed to improve this provisional quantification of each of them.

At low velocities it is known that the resistance varies as the square of the velocity (as it would at all velocities in an incompressible fluid), but two distinct cases may be noticed depending on the shape of the resisting body. If this has what, in a ship, would be called a fine run, that is, if the "after" part of the body tapers very gradually, so that the stream lines follow its contours, any resistance experienced by it is due to surface friction only. On the other hand, if the hinder part of the body is flat or tapers quickly, the stream lines leave the surface, and the body carries behind it a wake made up of a complex system of eddies whose formation requires a continuous expenditure of work.

The resistances considered in this paper are those of bodies which form a wake. One of the simplest cases is that of a plane moving in the direction of its normal. This, as a two-dimensional problem, has been solved—by Kirchhoff and by Lord Rayleigh—on the assumption that stream lines and wake are separated by a surface of discontinuity, the curvature of which is settled by the consideration that the pressure throughout the wake must be the same as the pressure in the distant parts of the fluid. The corresponding solution in three dimensions has not yet been effected.

The two-dimensional solution would apply accurately to the case of the

resistance of a long lamina in air moving slowly, if the space occupied by the theoretical wake and bounded by the surface of discontinuity was filled by a solid with a surface devoid of friction.

In the real case, however, the fluid wake is not at the pressure of the distant fluid, because, as shown in fig. 1, the eddies formed at the edge are
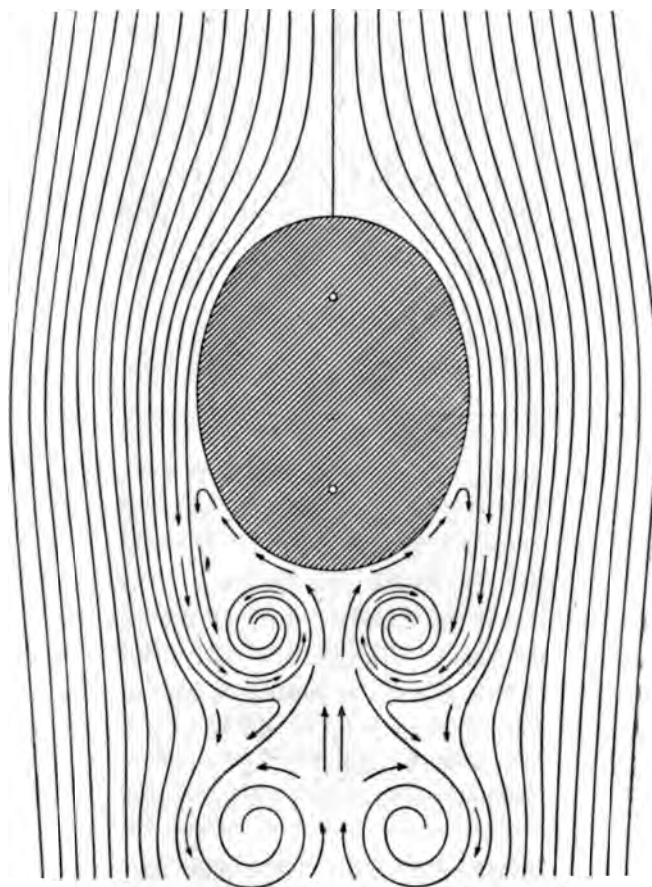
Fig. 1.

for ever wrapping up and drawing out from behind the plane part of the fluid which is found there. In consequence of this, fluid in the wake is not at rest relatively to the plane, but in its central part is flowing towards the plane to make good the loss of fluid abstracted by the eddies at its sides.

It must be noticed that the eddies in the wake are not of the nature of vortices in which each filament has the same velocity potential, but consist of a kind of sandwich-like structure, about half the fluid belonging to each

.eddy being derived from the interior of the wake and half from the general :stream outside. In two dimensions the formation of the eddies is a discon-tinuous process. In fig. 2, a, b, and c, illustrate their gradual growth, in (a) the eddy is just beginning to form at the edge of the plane, in (c) the growth
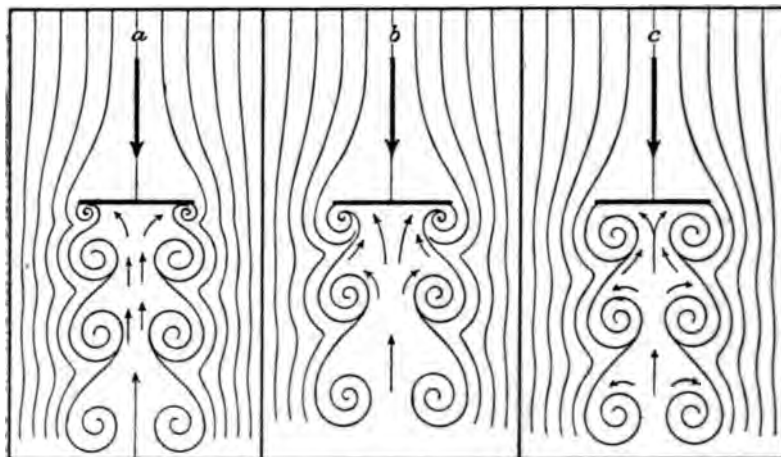
Fig. 2.

has proceeded until it impedes the forward flow of the wake which is neces-sary to feed it. When this stage is reached, the full-grown eddy breaks away and joins the procession of eddies forming the margin of the wake.

In three dimensions the eddies may be produced continuously, being in different stages of growth at different parts of the perimeter of the body behind which they are formed. In this case they either appear in the wake as a spiral* (see fig. 3), or, if the circumstances are such as to favour the inception of the eddy at some one point of the body, a current will be formed in the direction of the axis of the eddy.†

The rate at which eddies are produced has an important bearing on many natural phenomena.

In the two-dimensional problem the eddies may be formed symmetrically and simultaneously at the two edges, or alternately, in which latter case the wake consists of a series of alternate right-handed and left-handed eddies, fig. 4. If the wake-forming body is supported laterally, so that its natural period at right angles to the direction of the stream is t, then if the flow of the stream and dimensions of the body are such that the rate of eddy formation approaches t, the body will oscillate laterally with an amplitude increasing until the natural extinction balances the work done.

* Traces of the spiral may be seen in the shadow photograph, fig. 7.

† These phenomena are best examined by intermittence illumination, using a rate of intermittence slightly different from that of the eddy formation.
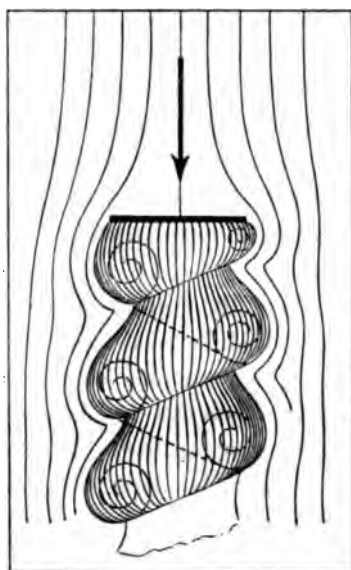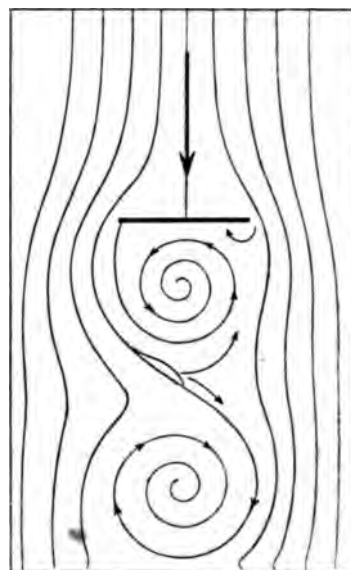
Fig. 3.   Fig. 4.

To this cause are due the vibrations of an Æolian harp string, and many other examples might be given.

The motion of the fluid in the wake is so complicated that it seems hopeless to treat it mathematically except in a statistical manner, and even for this data are at present wanting. It is known, however, that for low velocities in air the pressure on the hind surface of a plane is less than the general pressure in the fluid by about half the excess of pressure on the front surface.

As speed increases and approaches the velocity of sound, the negative pressure increases, because, apart from the question of supply to the eddies, the gas can only follow the plane at a reduced pressure, and when the velocity reaches 2400 f.s. about (in air) the negative pressure is equal to one atmosphere, and the hind surface is covered by a vacuum.

The negative pressure on the hind surface will be hardly affected by the shape of the front, hence, as one of the elements of resistance, we shall have a term which at first increases as the square of the velocity, grows rapidly as the velocity approaches that of sound, and at rather over 2400 f.s. becomes constant and equal to 1 atmosphere.

Next, as to the resistance of the head. I will suppose in the first place that the head is of such a shape that it would, in an incompressible fluid, get the full dynamic head due to the velocity over its whole surface.* (In an

* A plane fulfils this condition nearly, but not quite, as there is a small loss of pressure at the margins.

incompressible fluid the resistance of any other shape would be some constant fraction of this.)

Lord Rayleigh gives (in a paper on the Resistance of Fluids)[*] a formula for the head resistance of such a body as that just mentioned in an elastic gas (in which the pressure and density are connected by the equation $p/p_0 = (\rho/\rho_0)^{\gamma}$). This formula makes the resistance per unit area equal to the pressure required to cause a gas to flow from a vessel with the given velocity.

When we come to actually draw the curve which the formula represents, and compare it with the results of experiment, it will be seen that the two do not agree, and this not in the magnitude of the resistance only, but in general character. The adiabatic formula gives pressures which increase with the velocity much more rapidly than the pressures found by experiment, and I think the reason for this is that the formula credits the moving body with the energy required to pass through air at the maximum density with the prescribed velocity, whereas in the real case the density of the gas is the ordinary atmospheric density, and the body merely pushes a small cap of condensed air in front of it.

It must, I think, be admitted that some central part of this cap is raised to the full adiabatic pressure, but that part must extend over only a small fraction of the whole area, and that fraction itself must be a function of the velocity, and so that the law of resistance will be altered as well as the total amount. This is illustrated in fig. 5, where the curve A is the adiabatic resistance and B the resistance found by experiment; C represents $\frac{1}{2}\rho v^2$ (the
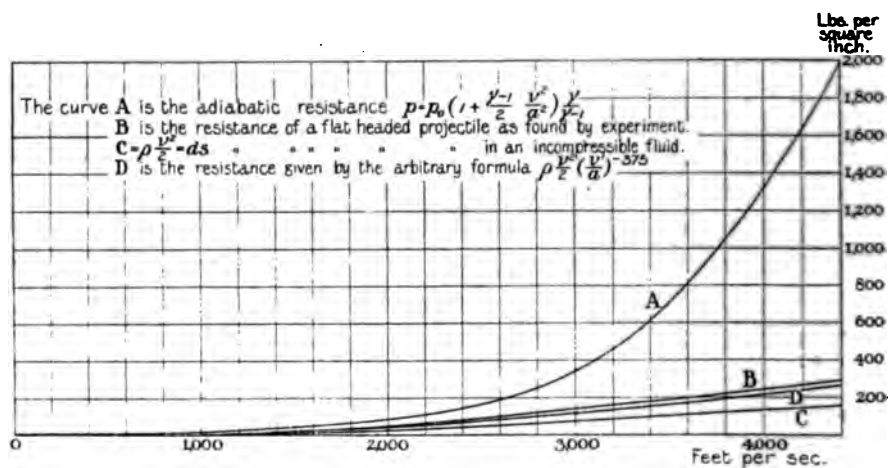
Fig. 5.

* 'Phil. Mag.,' Dec., 1876.

resistance which would be experienced per unit area in an incompressible fluid), and D is computed by the arbitrary formula $\frac{1}{2}\rho v^2 (v'/a)^{0.375}$.

In this latter formula, v' is the velocity with which a wave is propagated in the air immediately in front of the body and in the axis of the motion.

This velocity is the same as the velocity of the body when that exceeds the velocity of sound in the undisturbed gas, and it will be noticed that the pressure given by this formula, plus one atmosphere (on account of the defect pressure at the tail end), agrees well with experiment from velocities 2400 to 4500, beyond which I have not gone.

The diagram shows that the experimental resistance, although greater than $\frac{1}{2}\rho v^2$, is nearer to it than to the adiabatic pressure.

If we subtract $\frac{1}{2}\rho v^2 + p_0$ from the experimental value of the resistance, it is obvious that the difference (shown by the curve Z, fig. 9) is approximately a parabola whose ordinates are given by constant $X(v-a)^2$; and this element of resistance may be attributed to the force required to generate the waves which accompany the body when its velocity is greater than the velocity of sound.

The best evidence as to the nature of the waves in question may be drawn from the shadow photographs of rifle bullets taken by Mr. C. V. Boys.

One of these photographs (reproduced by permission in fig. 6) shows
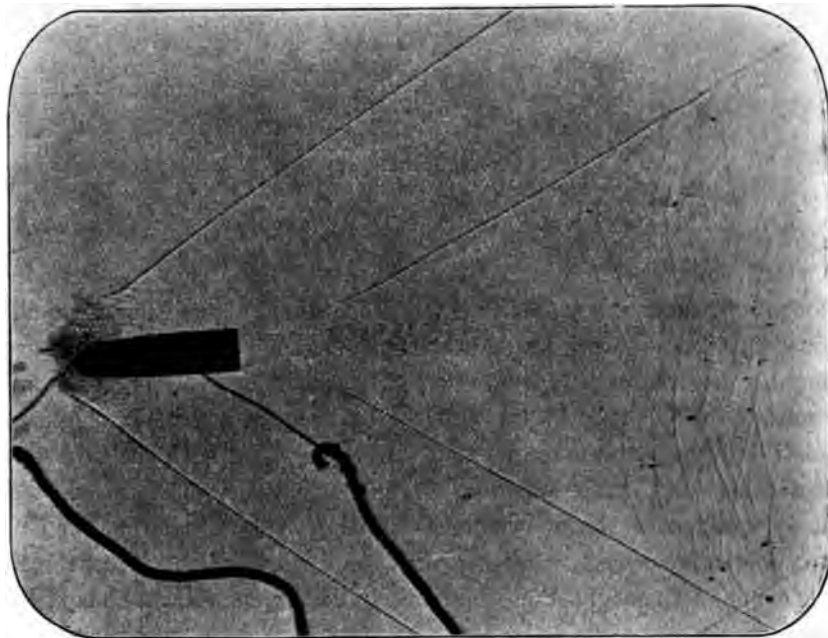
FIG. 6.—Photograph (by Professor C. V. Boys) of 0·303 rifle bullet at 2000 f.s.

a bullet travelling at about 2000 f.s. Accompanying it are two quasi-conical wave sheets having the same axis. The angle of the cone, of course, depends on the ratio of the velocity of the bullet to the velocity of sound, and the angle must be such that the velocity of the bullet resolved normal to the wave surface is equal to the velocity of sound in the gas in the condition as to pressure, density, etc., which obtains at the position through which the normal is drawn. The curvature, therefore, of the generating lines of the surfaces indicates that the conditions of the surrounding air are changed for a distance which is considerable, compared with the dimensions of the bullet.

The very sharp delineation of the wave in the photographs does not really imply an equally rapid change in the density at the wave surface, as may be seen from fig. 7, which is a shadow photograph of a heated tube.
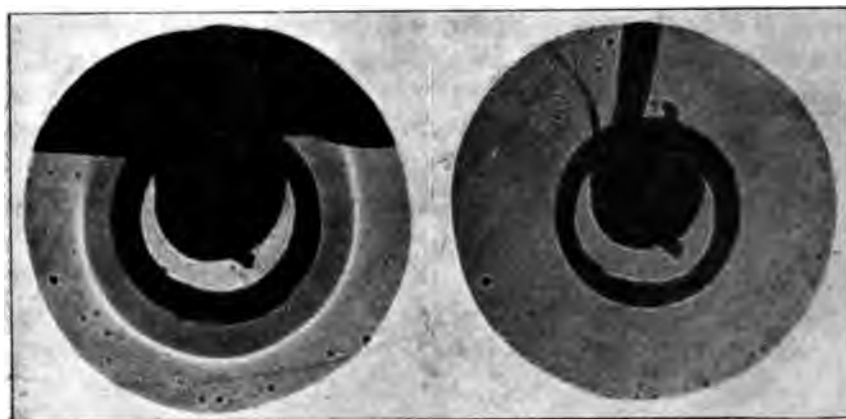
Fig. 7.

A small source of light was placed about 10 feet from the tube in the prolongation of its axis. The tube itself contained a small heating coil, and shadow photographs were taken at various distances with the tube raised to different temperatures. In fig. 7 the right-hand half of the picture is merely the geometrical shadow of the tube at ordinary atmospheric temperature. The left-hand half was taken in the same position but with the tube heated.

It will be seen that the warming of the air near the tube has deflected the light outwards, so as to somewhat magnify the shadow, and that the shadow is surrounded by a bright ring in which the deflected light is concentrated, but it cannot be thought that this ring indicates an abrupt change in the temperature of the air.

The varying temperature of the gas causes it to act on the beam of light

as a curved prism would, and to deflect the rays from the hotter to the cooler part of the air. In the analogous case of the bullet waves, the tendency is for the rays to be deflected towards the denser air.

Turning again to fig. 6, we see that both in the wave which precedes and in that which follows the bullet, the bright line is behind the dark one, showing that in both the most rapid change in the condition of the air is from a low to a higher density, that is, that both waves have steep fronts and that the pressure rises more quickly than it falls.

The origin of the wave in front of the bullet is obviously the compression of the air by the rapid motion, but it does not at first sight appear why a wave of compression should be set up well in its rear. This stern wave does not begin to show until the velocity is a good deal higher than the velocity of sound, and is caused by the closing together of the streams after they have passed the end of the bullet behind which, at such velocity, they leave a nearly vacuous space, plainly shown in all the photographs in which the stern wave appears. It will be noticed that the stern wave has its origin at the place where the wake is narrowest. An analogous phenomenon may be seen in water when a stream flows past an obstruction at such a speed as to leave a clear space behind it, the streams, as they meet again from either side, then mounting in a formidable-looking wave.

On the whole, therefore, it seems that the resistance of a body moving in a compressible gas may be represented as the sum of three terms, namely :—

(1) The positive pressure on the head (X) (treating the fluid as incompressible).

(2) The negative pressure on the tail (Y).

(3) The force necessary to generate the waves (Z).

The work done by (1) or (2) remains as velocity in the fluid forming the wake, and the wave-making energy, of course, travels along into space with the wave.

X varies as the square of the velocity. Y depends, in the first instance, on the difference of pressure which must exist between two regions if air is to flow from one to the other with the velocity of the bullet; the higher pressure being in this case the pressure of the atmosphere, but, owing to the conditions in the wake, the simple expression for this difference does not apply.

The wave-making resistance (Z) depends on $(v-a)$, and is apparently proportional to the square of that quantity.

I am not aware that any dynamical solution has been found for the

three-dimensional problem concerning the motion which would be set up in an elastic gas by the passage through it of a small region in which a constant pressure was maintained differing from the general pressure in the gas, when that difference is not small. Earnshaw's investigations, however, regarding plane waves of finite amplitude may be applied to the case of the resistance experienced by a frictionless piston moving in an infinitely long tube filled with gas.

Earnshaw shows that where the velocity of the gas is v' the pressure is $p_0 e^{v/a}$, and this indicates that the piston will drive in front of it a pond of condensed air at pressure $p_0 e^{v/a}$ whose length, measured from the piston, increases at the rate $v_0 \rho_0 / \rho$, but of course the projectile cannot carry with it an ever-growing cap of condensed air.

Assuming that the resistance of a projectile can be represented by the sum of the three terms X, Y, and Z, we can determine the constants in X and Z for flat-headed projectiles from the experimental results at velocities over 2400 f.s.,* for above this speed Y is constant and equal to 1 atmosphere.

If there were reliable data for the resistance of flat-headed projectiles down to 1100 f.s., we could at once, knowing X and Z, determine also, so far, the form of Y; but such data regarding flat heads are wanting.† We can, however, get at Y indirectly, for the resistance of pointed projectiles is known with considerable exactness up to velocities of 3500 f.s., and by comparing the resistance of the pointed and flat-headed projectiles at velocities above 2400 f.s., the reduction in the coefficients in X and Z due to the pointed form can be found, and then Y, which is unaffected by the shape of the head, can be found from the experiments on pointed projectiles.

The behaviour of the ordinary cup anemometer shows that at moderate speeds the ratio of the head resistance of the convex, to that of the concave, hemisphere is of the order of 1/4, and the coefficient $\frac{1}{4}$ seems to apply fairly to the relation between the head resistance of pointed and flat-headed projectiles at high speeds.

Using $\frac{1}{4}$ as the coefficient for the resistance of the pointed head, I find that the wave-making coefficient must be multiplied by about 1/5, owing to the change of shape, and that in a pointed projectile the resistance is fairly well expressed in C.G.S. units by the equation

$$R = \tfrac{1}{4}\rho_0 \tfrac{1}{2} v^2 + (1-A)^{0.354} + 1.35 \times 10^{-7} (v'-a)^2, \qquad (1)$$

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* 'Roy. Soc. Proc.,' Nov. 17, 1904, "Air Resistance."

† Most of the experiments on this subject have been made with the corner of the flat head rounded off, which leaves the effective area doubtful.

the corresponding equation for flat heads being

$$R = \rho_0 \tfrac{1}{2} v^2 + (1-A)^{0.354} + 7{\cdot}5 \times 10^{-7} (v'-a)^2. \tag{2}$$

Here ρ_0 = the density of the undisturbed air.

p_0 = „ pressure „ „ .

$A = \left(1 - \dfrac{\gamma-1}{2}\dfrac{v^2}{a^2}\right)^{\gamma/\gamma-1}$, so that $1-A$ is the resistance.

v' = the velocity of sound in the air just in front of the projectile, and is equal to v when $v' > a$.

These curves are plotted in figs. 8 and 9 (pp. 272 and 273) respectively, and the corresponding experimental values are marked by dots.*

One of the most remarkable features of the resistance curve for pointed projectiles is, that for velocities ranging from that of sound up to 3000 f.s. it is almost a straight line which, if produced, would cut the axis of abscissæ at a point where the velocity is about 850 f.s.

In a future paper advantage will be taken of this to find a simple formula giving the distance which any shot will traverse in a given time.

To determine the resistance of the air at quite low velocities, experiments have been made by many investigators, including the late W. Froude (in 1870, about) and Professor Langley, but most recently by Dr. Stanton at the National Physical Laboratory.

The resistance, of course, varies as the square of the velocity, and the coefficients formed for v^2 in C.G.S. units vary from $8{\cdot}68 \times 10^{-7}$ (Froude) to $6{\cdot}55 \times 10^{-7}$ (Stanton).

I think it should be noticed that Dr. Stanton's coefficient is almost exactly $\tfrac{1}{2}\rho$. It is the lowest value found by any experimenter, too low in fact, since, if correct, it would indicate that there was scarcely any negative pressure on the down stream side of the planes he used.

Further experiments are desirable in which the pressure on the up and down-stream side shall be measured separately, and this both for high and low velocities. I have reason to believe that an apparatus might be made which, for a moderate expenditure of power (about 10 horse power), would supply a continuous stream of air about 6 inches in diameter flowing with a velocity of over 1000 feet per second, and although the current would probably be a turbulent one, I should not expect that the resistance experienced by a body placed in it would, if averaged for a few seconds, differ greatly from the resistance in a smoothly flowing stream of the same mean velocity.

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* In the diagrams, the units employed are pounds per square inch and feet per second.

At velocities of this order, the resistance is of the order of pounds per square inch (something like 10 lbs. per square inch for a plane at the velocity of sound), hence very measurable forces would be exerted on bodies

Resistance of a Pointed Projectile.

$$X = \tfrac{1}{4}\rho \frac{v^2}{2}$$

$$Y = p_0(1-A)^{.354} \quad \text{where } A = \left(1 - \tfrac{\gamma-1}{2}\frac{v^2}{a^2}\right)\frac{\gamma}{\gamma-1}$$

$$Z = 1.69 \times 10^{-6}(v'-a)^2$$

$$a = \text{velocity of sound}$$

$$R = X + Y + Z$$

The crosses x shew the results of experiment.
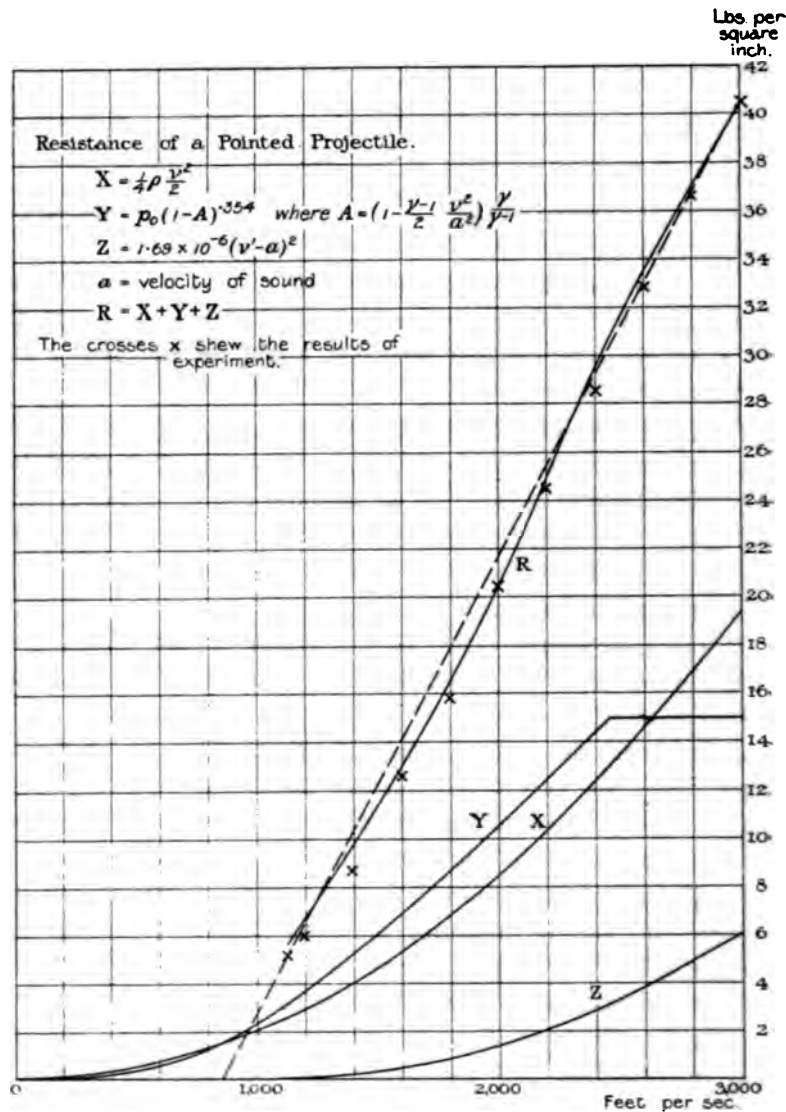
Fig. 8.

small compared to the diameter of the stream, and therefore not influenced by the walls which confine it. Much interesting information might be obtained from experiments of this nature.

Resistance of Flat-headed Projectile.

$$X = \rho \frac{v^2}{2}$$

$$Y = p_o (1-A)^{.354} \quad \text{where } A = \left(1 - \frac{\gamma-1}{2}\frac{v^2}{a}\right)\frac{\gamma}{\gamma-1}$$

$$Z = 9.45 \times 10^{-6}(v-a)^2 \quad \text{where } a = \text{velocity of sound.}$$

$$R = X + Y + Z$$

The crosses x shew the results of experiment.
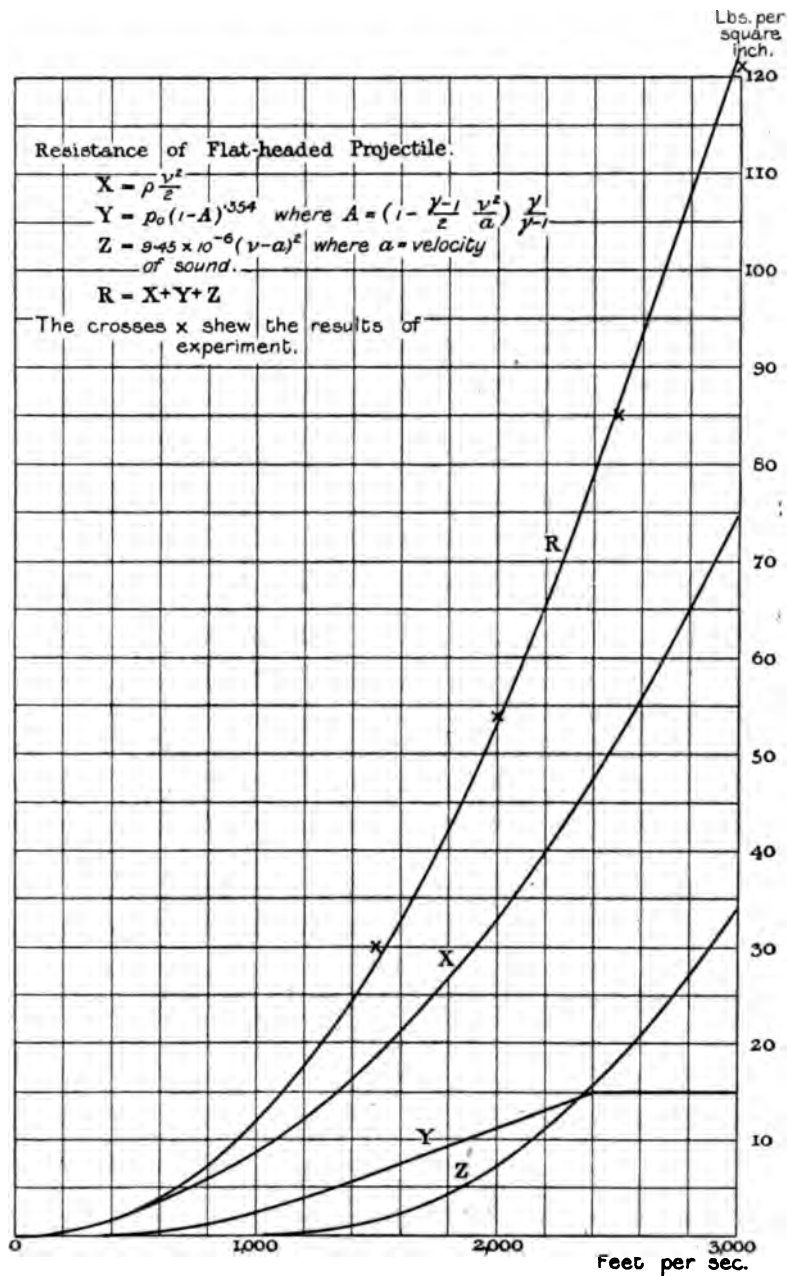
Fig. 9.

Space described in a Given Time by a Projectile Moving in Air.

By A. MALLOCK, F.R.S.

It was pointed out in the paper on " The Resistance of Air," recently read before the Society, that for velocities from 1100 to 3000 feet per second, the resistance curve of a pointed projectile was approximately represented by a straight line which, if produced, would cut the axis of abscissæ at $v = 850$ f.s. The equation of this line is

$$R = 2{\cdot}53 \, (v-v'),$$

where R is the resistance in pounds per square foot of cross-sectional area, the velocities being in feet per second, and where $v' = 850$ f.s. The retardation (f) of the shot is given by $f = \dfrac{2{\cdot}53g}{\rho l} (v - v')$, where ρ is the weight of the unit volume of material, and l the equivalent length of the projectile. (By equivalent length is meant the length of a cylinder of the same weight and density as the projectile.)

The quantity ρl is another, and for many purposes a more convenient, form of the ballistic coefficient, which is usually stated as w/d^2. It represents the mass of the projectile per unit area of cross-section on which the retardation acts.

From equation for f, it is easy to deduce a formula for the space traversed by the projectile in a given time, and in this paper I give a few examples of ranges in terms of time computed from it.

The formula for the distance s, traversed by the shot in time t is*

$$s = v't + \frac{u_0}{a} (1 - e^{-at}),$$

and for the remaining velocity

$$v_1 = v' + u_0 e^{-at},$$

where $v' = 850$ f.s. and $v = $ initial velocity $-v'$. It is easy to plot curves of s and v in terms of t from this formula, by making a table for e^{-x} and finding the times which correspond to the various values of x.

Three examples of such curves are appended in the diagram, viz., for 12-inch, 6-inch, and 0·303-inch projectiles. The results of actual practice

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* Let the straight line AC be the diagram of retarding force in terms of velocity, where OB $(= v_0)$ is the initial velocity and OA $(= v')$ is 850 f.s.

Space described in time
by A 12" projectile. Muzzle velocity 2,700 f.s. u_0= 1,850 a = ·0748 w = 850 lbs.
  B   6"   »   »   »   2,575 »   » ·1695   » » ·158   » = 100 »
  C ·303 »   »   »   2,080 »   » =1,230   » = 1·15 » = ·037 »

Thousand yards for A and B.
Hundred yards for C.

Full curves are calculated by the formula
range = $v't + \frac{u_0}{a}(1 - e^{-at})$
× Ranges found by experiment

Seconds for A and B, tenths of seconds for C.
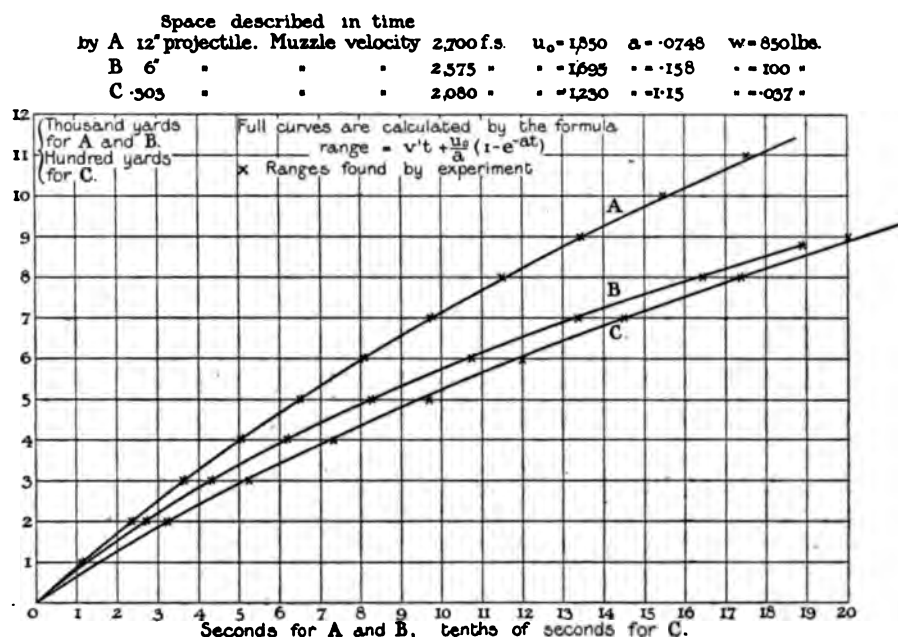
with the same projectiles are shown by the spots.   It will be seen that the results agree very closely with actual practice, so closely indeed as to be within the error of observation.

The equation of AC is $f = -a(v - v')$.   Put $v - v' = u$, $v_0 - v' = u_0$, so that $a = f_0/u_0$.
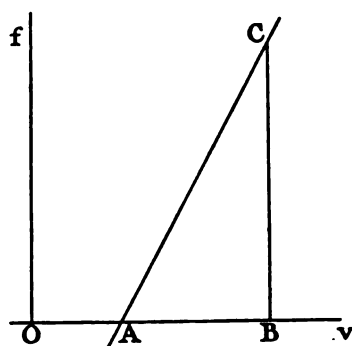
The negative velocity generated in time t by f is $\int f dt$.

Now $f = dv/dt = du/dt = -au$; hence $\log u = -at + c_1$. $\hspace{2cm}$ (1)

When $t = 0$, $u = u_0$ $\therefore c_1 = \log u_0$ and $u/u_0 = c^{-at}$ (1), $\therefore v = v' + u_0 c^{-at}$.   The distance s, traversed by the projectile in time t, is $\int v dt$, and $\int v dt = \int (v' + u)dt = v't + \int u dt =$

$v't - \frac{v_0}{a} c^{-at} + c_2$.   When $t = 0$, $s = 0$, $\therefore c_2 = u_0/a$, hence $s = v't + \frac{u_0}{a}(1 - c^{-at})$. $\hspace{1cm}$ (2)

Experiment shows that the resistance in lbs. per square foot is nearly represented

U 2

I think it is worthy of remark that this formula used with data derived solely from the weight and dimensions of the shot, together with the value for resistance above given, leads to results which are scarcely distinguishable from (but probably more accurate than) those obtained from actual firing, and this from the 12-inch shot, weighing 850 lbs., down to the 0·303-inch, which weighs 26,000 times less.

It remains, in order to construct a general formula for the range of all pointed projectiles, to find at what angle to the horizontal the trajectory must start in order that the shot may remain in the air for a given time.

This involves rather intricate questions relating to the effect which the spin of the rifled projectile has in keeping its axis nearly in the tangent to the trajectory, and will be touched on in another paper.

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by $2\cdot53\,u$. (The coefficient of u will vary slightly with the shape of the head of the projectile. The number $2\cdot53$ refers to an ogival head with a radius of ogive of two diameters. The coefficient for the 0·303 projectile is $2\cdot60$.) Now resistance÷weight of the projectile $= f/g$, so that $f = 2\cdot53\,gv/\rho l$, where ρ is the weight of a cubic foot of the material of the projectile, and l its "equivalent length"; hence, since $a = f_0/u_0$, $a = 2\cdot53\,g/\rho l$, or $81\cdot3/\rho l$ nearly. The dimensions of a, are T^{-1}, and $1/a$ is the time in which u is reduced in the ratio of e to 1. If the weight of the shot is given, ρl may be replaced by $4w/\pi d^2$, so that $a = 2\cdot53\,\pi d^2/4w$, or $6\cdot385\,d^2/w$.

On the Variation of the Pressure developed during the Explosion of Cordite in Closed Vessels.

By CHARLES H. LEES, D.Sc., F.R.S., Professor of Physics in the East London College, and J. E. PETAVEL, M.Sc., Lecturer on Mechanics in the University of Manchester.

It has been recently shown* that Sir Andrew Noble's observations† on the maximum pressure P developed by the explosion of cordite in an enclosure of constant volume can be expressed by the equation

$$P = \frac{c\rho}{1-b\rho}, \qquad (1)$$

where ρ is the gravimetric density of the charge in the vessel (0 to 0·6), *i.e.*, the quotient of the mass of the charge by the volume of the vessel, c is a constant whose value is 65·75 if pressure is measured in tons per square inch, and is 10,021 if measured in atmospheres, and b is equal to 0·641 the reciprocal of the density 1·56 of cordite.‡

Writing the mass of cordite M, its density σ, and the volume of the vessel v, we have

$$\rho = \frac{M}{v}, \qquad b = \frac{1}{\sigma},$$

and the equation becomes

$$P = \frac{c\dfrac{M}{v}}{1 - \dfrac{M}{\sigma}} = \frac{cM}{v - \dfrac{M}{\sigma}}.$$

Or if v_0 is the volume of the cordite, $M/\sigma = v_0$, and we get

$$P = \frac{cM}{v - v_0}; \qquad (2)$$

i.e., the maximum pressure developed is proportional to the mass and therefore to the volume of cordite used, and inversely proportional to the volume of the vessel initially unoccupied by cordite.

Since this holds for the maximum pressure, it is reasonable to suppose that

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* Petavel, 'Phil. Trans.,' A, vol. 205, p. 385.

† 'Proc. of Royal Inst.,' vol. 16, Part II, p. 329, 1900; also 'Text-book of Gunnery,' p. 99, 1901.

‡ The results given by Sir Andrew Noble for Cordite Mark I in 'Phil. Trans.,' A, vol. 206, p. 761, give c 73·5 and 11,200 respectively.

it holds throughout the explosion, *i.e.*, that if p is the pressure at any instant and m the mass of cordite consumed up to that instant,

$$p = \frac{cm}{v - v_0}. \tag{3}$$

Now it has been shown by Vieille[*] and by Noble[†] that cordite when once ignited is consumed in parallel layers. Hence if R is the radius of the cylinders of cordite used, r their mean radius at the instant when the pressure is p,

$$\frac{p}{P} = \frac{m}{M} = \frac{R^2 - r^2}{R^2} = 1 - \frac{r^2}{R^2},$$

if the burning at the ends of the cylinders be neglected. Hence

$$r^2/R^2 = 1 - p/P \quad \text{or} \quad r = R\sqrt{(1 - p/P)}.$$

If, then, from observations of the pressure as a function of the time, we determine r by this equation, we can deduce the law of variation of the speed of combustion $\left(-\dfrac{dr}{dt}\right)$ with p. This was done for 13 of the experiments described in 'Phil. Trans.,' A, vol. 205, p. 390, and the values of $\dfrac{dr}{dt}$, plotted against p. They were found to lie close to a straight line passing a little above the origin of pressure.

It seemed, therefore, worth while to calculate the consequence of taking the speed of combustions S as given by the equation

$$S = a_0 + ap, \tag{4}$$

where, from the position of the line found, it seemed probable that $a_0 =$ about 0·4 cm. per second, and $a =$ about 0·018 cm. per second per atmosphere, the pressure being measured in atmospheres.[‡]

If R is the radius of the cordite, ρ the gravimetric density of the charge, P the maximum pressure which would be generated according to equation (1), and if there were no cooling, we should have at the time t, at which the mean radius of the zones of combustion $= r$,

$$-\frac{dr}{dt} = a_0 + ap, \tag{5}$$

and

$$p = p_0 + P\left(1 - \frac{r^2}{R^2}\right), \tag{6}$$

* 'Comptes Rendus,' vol. 118, p. 346, etc.

† 'Roy. Soc. Proc.,' vol. 52, p. 129.

‡ This result was communicated verbally to the Society on February 14, during the discussion on Major Mansell's paper "On the Law of Burning of Modified Cordite," in which he gave an expression of the same form for the rate of combustion.

where p_0 is the pressure in the enclosure at the commencement of the explosion.

Differentiating (6) with respect to time, we have

$$\frac{dp}{dt} = -\frac{2Pr}{R^2} \cdot \frac{dr}{dt}$$

$$= \frac{2Pr}{R^2}(a_0 + ap)$$

$$= \frac{2P}{R}\sqrt{1 - \frac{p-p_0}{P}} \cdot (a_0 + ap).$$

Hence

$$\int \frac{dp}{(a_0 + ap)\sqrt{1 - \frac{p-p_0}{P}}} = \frac{2P}{R}t + \text{constant.} \qquad (7)$$

Let

$$a_0 + ap = \frac{1}{z}, \quad i.e., \quad p = \frac{1}{a}\left(\frac{1}{z} - a_0\right),$$

then

$$\frac{adp}{a_0 + ap} = -\frac{dz}{z},$$

and

$$\int \frac{dp}{(a_0 + ap)\sqrt{1 - \frac{p-p_0}{P}}} = -\int \frac{dz}{az\sqrt{1 + \frac{p_0}{P} - \frac{1}{Pa}\left(\frac{1}{z} - a_0\right)}}$$

$$= -\frac{1}{a\sqrt{1 + \frac{p_0 + \frac{a_0}{a}}{P}}} \operatorname{argcosh}\left(2\frac{p_0 + \frac{a_0}{a} + P}{p + \frac{a_0}{a}} - 1\right).^{*}$$

Hence

$$\operatorname{argcosh}\left(2\frac{p_0 + \frac{a_0}{a} + P}{p + \frac{a_0}{a}} - 1\right) = -\frac{2aP}{R}\sqrt{1 + \frac{p_0 + \frac{a_0}{a}}{P}} \cdot t + \text{constant.}$$

If we measure t from the instant at which the explosion commences, $p = p_0$, when $t = 0$.

Hence the equation becomes

$$\operatorname{argcosh}\left(2\frac{p_0 + \frac{a_0}{a} + P}{p_0 + \frac{a_0}{a}} - 1\right) - \operatorname{argcosh}\left(2\frac{p_0 + \frac{a_0}{a} + P}{p + \frac{a_0}{a}} - 1\right)$$

$$= \frac{2aP}{R}\sqrt{1 + \frac{p_0 + \frac{a_0}{a}}{P}} \cdot t, \qquad (8)$$

* Tables of these hyperbolic functions may be found in 'Dale's Mathematical Tables.'

i.e.,

$$2\frac{p_0+\frac{a_0}{a}+P}{p+\frac{a_0}{a}}-1 = \cosh\left\{\operatorname{argcosh}\left(2\frac{p_0+\frac{a_0}{a}+P}{p_0+\frac{a_0}{a}}-1\right)-\frac{2aP}{R}\sqrt{1+\frac{p_0+\frac{a_0}{a}}{P}}.t\right\},$$

or

$$p+\frac{a_0}{a} = 2\cdot\frac{p_0+\frac{a_0}{a}+P}{1+\cosh\left\{\operatorname{argcosh}\left(1+\frac{2P}{p_0+\frac{a_0}{a}}\right)-\frac{2aP}{R}\sqrt{1+\frac{p_0+\frac{a_0}{a}}{P}}.t\right\}}. \quad (9)$$

From (9) it follows that the total time T occupied by the explosion is given by

$$\frac{2aP}{R}\sqrt{1+\frac{p_0+\frac{a_0}{a}}{P}}.T = \operatorname{argcosh}\left(1+\frac{2P}{p_0+\frac{a_0}{a}}\right);$$

i.e.,

$$T = \frac{R}{2aP\sqrt{1+\frac{p_0+\frac{a_0}{a}}{P}}}\operatorname{argcosh}\left(1+\frac{2P}{p_0+\frac{a_0}{a}}\right)$$

$$= \frac{R}{2a\frac{c\rho}{1-b\rho}\sqrt{1+\frac{p_0+\frac{a_0}{a}}{\frac{c\rho}{1-b\rho}}}}\operatorname{argcosh}\left(1+\frac{\frac{2c\rho}{1-b\rho}}{p_0+\frac{a_0}{a}}\right) \quad (10)$$

in virtue of (1).

Hence the time taken by the explosion is, for the same initial pressure and gravimetric density, proportional to the radius R of the cordite used, *i.e.,*

$$T \propto R. \quad (11)$$

Considered as a function of p, dp/dt will have its maximum for a value of p determined by the equation

$$\frac{d^2p}{dp.dt} = 0, \quad \textit{i.e.,} \quad a\sqrt{1+\frac{p-p_0}{P}}-\frac{a_0+ap}{2P\sqrt{1-\frac{p-p_0}{P}}} = 0,$$

i.e., when

$$p = \tfrac{2}{3}\left(p_0+P-\frac{a_0}{2a}\right),$$

i.e., when

$$p = \tfrac{2}{3}P \text{ approximately}; \quad (12)$$

that is when the actual pressure is approximately two-thirds of the maximum

pressure. The maximum rate of increase of the pressure is therefore given by the equation

$$\text{maximum } \frac{dp}{dt} = \frac{4\mathrm{P}a}{3\sqrt{3}.\mathrm{R}} \cdot \sqrt{1 + \frac{p_0 + \frac{a_0}{a}}{\mathrm{P}}} \cdot \left(p_0 + \frac{a_0}{a} + \mathrm{P}\right);$$

i.e., $\qquad\qquad \text{maximum } \dfrac{dp}{dt} = \dfrac{4\mathrm{P}^2 a}{3\sqrt{3}.\mathrm{R}} \text{ approximately;}$

that is proportional to the square of the maximum pressure attained, inversely proportional to the radius of the cordite used, and directly proportional to the pressure coefficient of the speed of combustion of the cordite.

The most severe test of the preceding theory is its power of reproducing the curves of variation of pressure with time during the course of an explosion. The available number of such curves free from oscillations of the
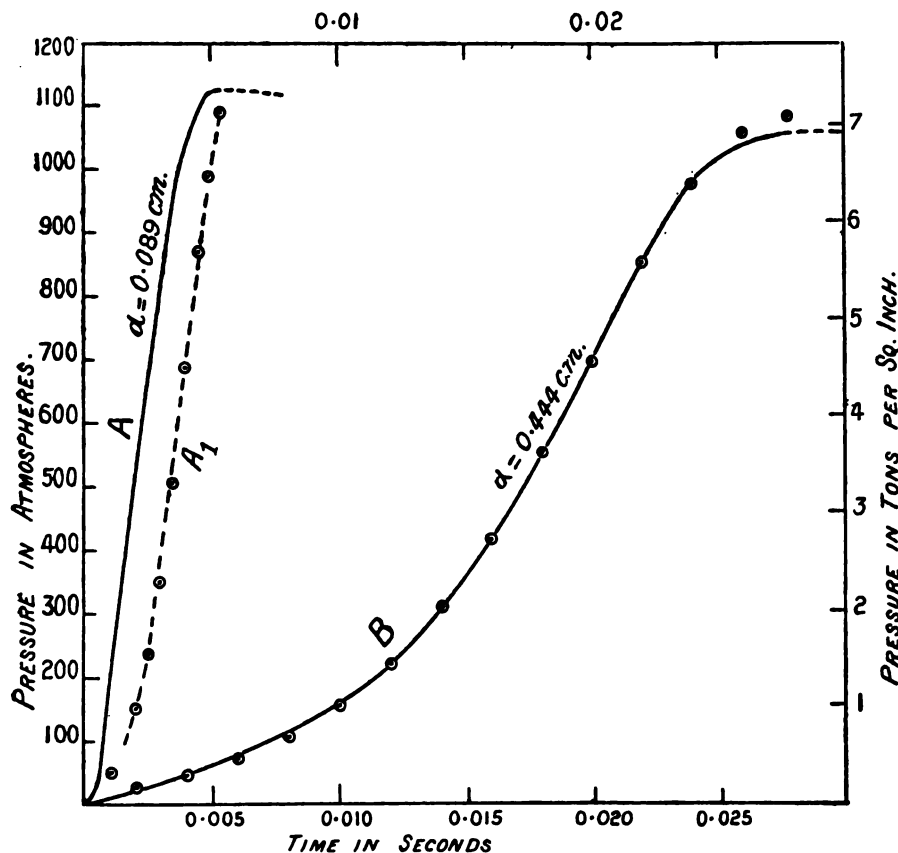
Fig. 1.—Time pressure curve for cordite Mark I fired in a closed vessel at a gravimetric density of 0·1. The curves are reproduced from photographic records. The separate points are calculated by formula (9).

recording instrument is small, and they relate to charges of gravimetric densities not exceeding 0·15.*   Several of these results have been compared with the above expression, and the agreement found in each case is very close.

It may be illustrated by two typical examples, in both of which the gravimetric density is 0·10, but in A the diameter of the cordite is 0·089 cm., and in B 0·444 cm.   In curve B the agreement is entirely satisfactory.   Curve A, however, is in advance of the calculated points by about one thousandth of a second.

Now, the chronographic determinations in experiments of this kind give *relative* times to a high degree of accuracy, but the zero from which time should be counted is not so easily fixed.   In the present case a zero error of one or two thousandths of a second might well have occurred.   Assuming this to have been the case, we have added a constant of 0·0013 second to the abscissæ of A, and so obtain the dotted curve A_1, which follows closely the calculated points.

A further test of the theory may be found in the values of the time required for the pressure to reach its maximum.   These times, as determined by Petavel at various gravimetric densities and for various diameters of cords, are shown in fig. 2.

The calculated values coincide exactly with the measurement of the
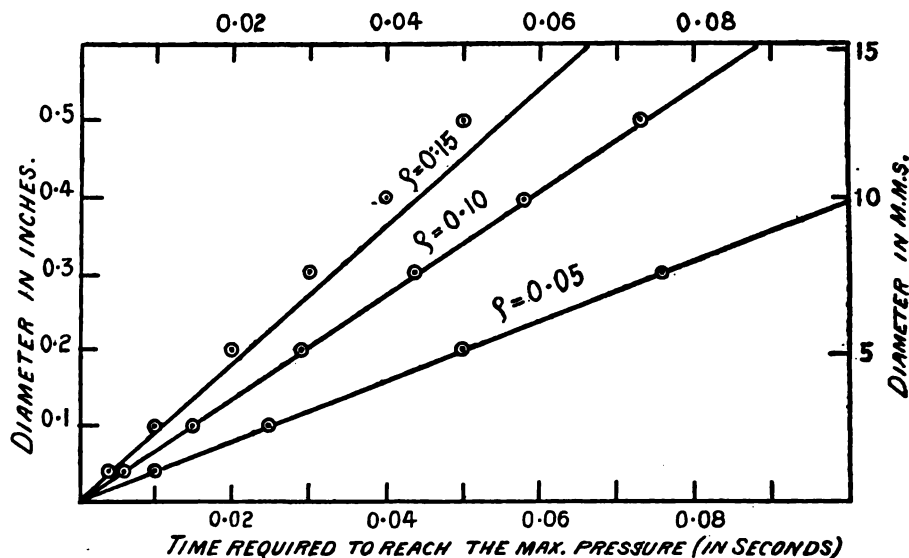
Fig. 2.—Time required to reach the maximum pressure. The curves are drawn from experimental determinations. The separate points represent the values calculated by formula (10).

* Petavel, 'Phil. Trans.,' A, vol. 205, pp. 390—398.

photographic records for gravimetric densities of 0·05 and 0·1, but for 0·15 they show a certain departure, ranging from one thousandth of a second for the fine cord and five thousandths for the largest.

This divergence may probably be attributed to the difficulty of fixing experimentally the zero from which the time should be counted. It is easy to time the instant of firing, *i.e.*, the instant at which the cordite is surrounded by the flame produced by the igniting charge, but this time does not coincide with the time of ignition of the charge. Although surrounded by an intensely hot flame, the explosive requires some thousandths of a second before it bursts into flame. This time, of course, depends on the specific heat of the explosive and its ignition temperature. That this time is by no means inappreciable may be judged by the fact that a rod of cordite of large diameter may be passed comparatively slowly through a Bunsen flame without igniting.

The above comparisons are, we think, sufficient to show that the formula (9) represents the experimental data with sufficient accuracy, and it may be of interest to use it to determine the form of the pressure-time curves for higher pressures, under which it has been found difficult to free the curve determined experimentally from the oscillations due to the recording instrument.

In fig. 3 this curve is plotted for gravimetric densities of 0·1, 0·25, and
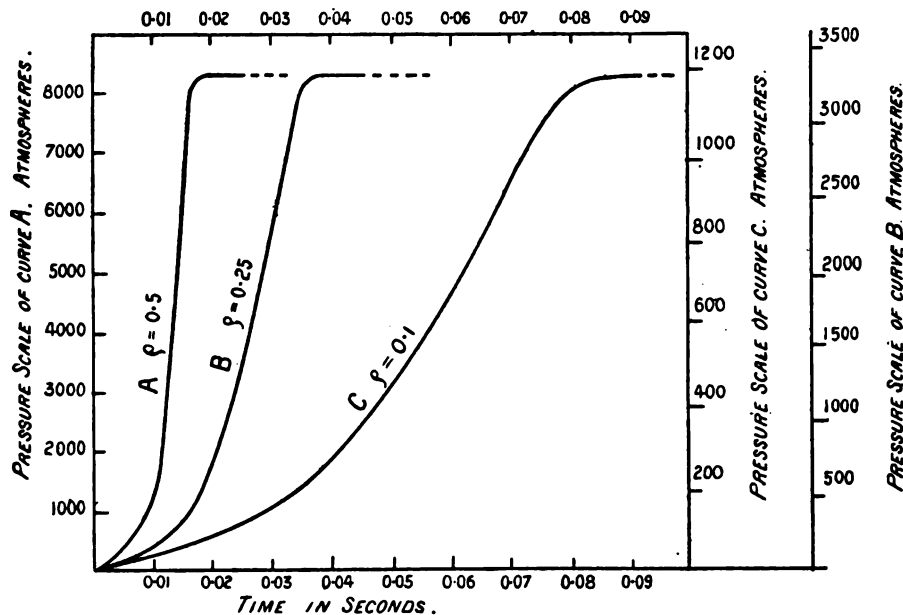
Fig. 3.—Showing the variation in the shape of the combustion curve with increasing gravimetric density. The three curves are calculated from formula (9), taking $c = 11,200$, $a_0 = 0·4$, $a = 0·018$; they are reduced to the same maximum ordinate to show clearly the relative change in shape.

0·50 of cordite of diameter 0·6-inch, the three curves being reduced to the same maximum ordinate in order to show the relative change in shape.

The principal facts are at once noticeable. The first, *i.e.*, the considerable increase in the velocity of the explosion, with increase of gravimetric density, is, of course, well known.

The second, *i.e.*, the change in shape of the curve, has considerable practical importance. Whereas at very low gravimetric densities (0·10) the combustion curve is made up of three parts which are of nearly equal importance, *i.e.*, a comparatively slow initial rise, a central rapid, and a final slow rise; at higher gravimetric densities (0·25 and 0·50) the central portion preponderates.

The pressures developed during the ignition period are too small to greatly affect most ballistic problems, in which the effective densities are of the order (0·2). These considerations justify the method adopted by Noble, who, for practical purposes, takes the zero of time at the commencement of the central portion of the curve.

Summary of Results.

(1) As most of the modern explosives used in ballistics follow the law of combustion by parallel surfaces, from what precedes it appears that their properties may be defined by four constants, which may be determined without difficulty by direct experiment.

(2) The constants b and c (of formula 1) fix the maximum pressure which will be attained under any given charging density. The constants a_0 and a (of formulæ 4 and 9) measure the rate of combustion and determine the time which elapses between the ignition of the charge and the development of the maximum pressure.

(3) When the explosive is made up in a cylindrical form, the time occupied by an explosion for the same gravimetric density is proportional to the diameter of the cylinder.

(4) The rate of increase of the pressure is most rapid when about two-thirds of the maximum pressure has been attained.

(5) The maximum rate of rise of pressure per second is equal approximately to $1·54a$ into the square of the maximum pressure in atmospheres divided by the diameter of the cordite in centimetres.

(6) When the explosion is fired under a high gravimetric density, the "effective" time of combustion may for practical purposes be taken as equal to the time required if the combustion proceeded always at its maximum rate.

For cordite Mark I this time is given by $T = 36\,D/P$ if the diameter D is measured in centimetres and the maximum pressure P in atmospheres, or $T = 0\cdot6\,D/P$ if the units are inches and tons per square inch.

Throughout the above investigation the cooling effect of the walls of the containing vessel during the combustion has been taken as small enough to be neglected.

Experiments with Vacuum Gold-leaf Electroscopes on the Mechanical Temperature Effects in Rarefied Gases.

By J. T. BOTTOMLEY, M.A., LL.D., D.Sc., F.R.S., and F. A. KING.

The following is intended to be a preliminary notice of some striking mechanical effects which we have observed in the gold leaves of vacuum electroscopes, and which, at first sight, might be taken to simulate electrification of bodies by light and radiant heat.

Experiment 1.—The first indications which presented themselves to us, of the existence of the peculiar effects which we are about to describe, were obtained while we were experimenting with a " radium clock," constructed much as described by the Hon. R. Strutt, F.R.S.* We have set up this apparatus for the purpose of carrying out secular observations, and in order to find, if possible, whether the activity of the radium seems to diminish with time.

The radium clock, as is well known, is practically a gold-leaf electroscope, contained in an outer vessel highly exhausted, in which a small glass tube containing some radium, and with its outer surface smeared with an aqueous solution of phosphoric anhydride, is connected metallically to the gold leaves. Two metallic plates, with connections passing to the outside through the glass cover of the electroscope, are placed on the two sides of the gold leaves; and the leaves are long enough to touch these plates when their divergence reaches a certain amount. As the β-rays of the radium emanation escape, the α-rays electrify the gold leaves, which then diverge; and, diverging, they come in contact with the side plates. They are then discharged, and fall together again; but again become electrified as before.

* Strutt, ' Phil. Mag.,' November, 1903 ; Rutherford's ' Radio-activity,' 2nd edition, p. 122.
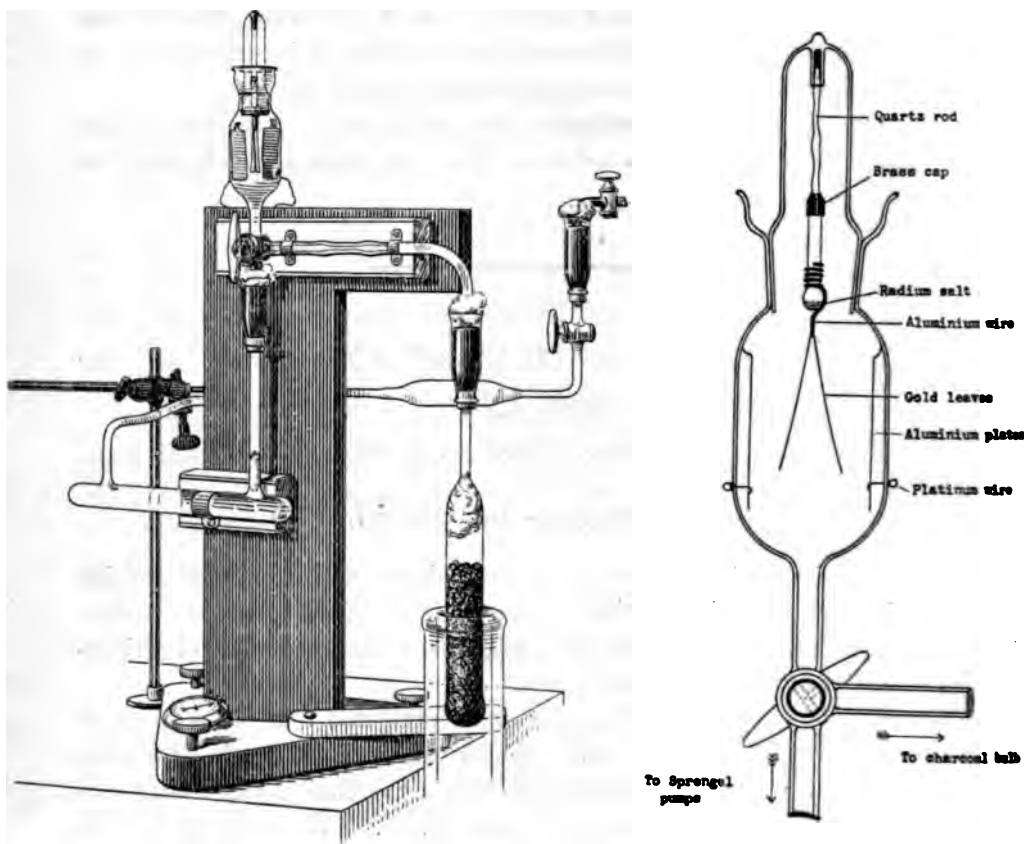
General View of "Radium Clock" Apparatus and Section of the "Clock."

A periodic action thus goes on, the gold leaves alternately diverging and collapsing. In the "clock" which we have constructed, and with a vacuum of 1/20 M,* the period of the gold leaves is about $3\frac{1}{4}$ minutes.

While observing the radium clock, and endeavouring to improve the vacuum of the apparatus, a Bunsen burner which was being used was placed in rather close proximity to the clock. It had a long, powerful, flame, and it was observed, after a short time, that the gold leaves of the clock were apparently repelled by the flame.

It is impossible to make the gold leaves so symmetrical that they shall both strike on their respective fixed side plates at the same instant. One must strike first, and then both are discharged. In our case, that which we will call the "left hand" leaf, looking at the apparatus from what we will call the "front," had been striking first. The Bunsen burner was, by chance, standing on the "left." It was noticed that the leaves did not

* **M** denotes one-millionth of standard atmospheric pressure.

hang down symmetrically, as shown in fig. 1, but were repelled and hung as shown in fig. 2; and as their divergence increased the " right hand " leaf was the first to strike on its side plate, and it was found at the same time that the period of the clock was greatly increased.

fig.1.   fig.2.
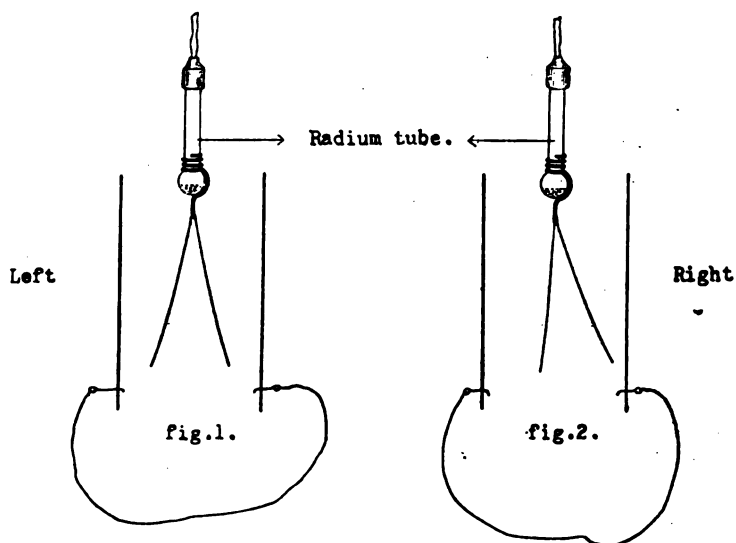
Experiment 2.—A common soldering bolt was next heated, sometimes to red heat, or almost to white heat, and later on to temperatures far below red heat but higher than that of the surrounding atmosphere, and it was found that, when this was brought near, the leaves of the radium clock behaved much as they did in the presence of the flame. The same effects were obtained when a spirit flame, or a candle flame, was used instead of a Bunsen burner.

Experiment 3.—Even the heat of the hand was found to be quite sufficient to cause repulsion of the gold leaves of the clock. By bringing up the warm hand close to the outside cover of the clock, the leaves could be driven slowly, first in one direction and then in the other, and they could in this way be prevented from striking on the side plates; thus the period of the clock could be greatly augmented. In one case which we have noted, the striking on the side plates was delayed, by alternately placing the hand to the right and to the left of the gold leaves, to such an extent, as to make an interval of 6½ minutes, the normal period of charge and discharge, at the time, being 3 minutes 4 seconds.

Experiment 4.—To try the effect of cold, a test tube was filled with water, and with the help of a vessel filled with liquid air, the water was frozen,

first, and was then cooled down nearly to the temperature of the liquid air. We had thus a bar of solid matter, having a great capacity for cold, and chilled to a very low temperature; and this was brought near to the clock, just as had been done with the flame, and with the bar of heated copper. When the bar of chilled ice was brought near to the leaves they were markedly attracted; and, in fact, the action of the chilled body appeared to be exactly the inverse of what we had observed in the case of the heated bar of metal.

Experiment 5.—When the clock was covered entirely with a cage made of fine brass gauze, and the gauze cage connected to a neighbouring gas pipe, the peculiar attraction and repulsion of the gold leaves was still observed, with but little diminution in intensity, when hot and cold bodies were presented, as described above.

The leaves, however, under these circumstances, were *unaffected when electrified rods of glass and sealing wax were brought near*, being protected by the presence of the wire gauze cover, as was shown by Faraday, in his Experimental Researches.

A great variety of experiments were also tried, but need not be described in detail here, on the effect of screens of metal, glass, mica, cardboard, paper, etc., also of liquids contained in a parallel sided cell and, lastly, of vacuum; the vacuum between the walls of a Dewar vessel for holding liquid air being used for this purpose.

To ascertain how far the phenomena observed might be attributed to heating and cooling effect, the region of air surrounding the radium clock was carefully explored with the help of a very sensitive thermo-electric junction. The result of this experimenting was to show that thermal radiations, which were almost too slight to be detected with the thermo-junction, could produce very marked effects in causing disturbance of the gold leaves.

It is to be expected that the radiometric forces investigated by Sir W. Crookes would be much in evidence in this arrangement, owing to the small mass and large surface of the leaves, and their contiguity. In fig. 2 the colder leaf is repelled from the warmer one, but the latter suffers reaction on both sides from the molecules of the gas, which it accelerates, and so remains in position. The long duration of the effects is a striking feature.

It was now determined to construct a special gold-leaf electroscope for the purpose of investigating the phenomena which these preliminary experiments pointed to; and, after several small electroscopes had been made, a convenient instrument was obtained, which may be described as

follows, and of which fig. 3 is a drawing. The essentials aimed at are:
(1) convenient dimensions; (2) perfect dryness of the interior; (3) high
exhaustion.

The electroscope is contained in an enclosure, made from a piece of glass
tubing $1\frac{1}{2}$ inches in diameter, drawn out at both ends to form tubes
e, e', fig. 3. A piece of thermometer tubing t is sealed on to the neck e,
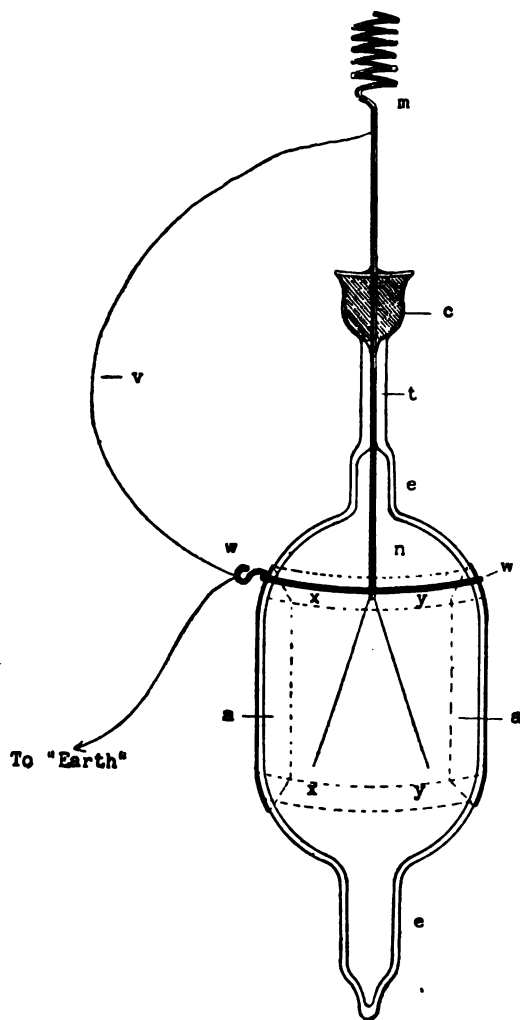
Fig. 3.

and the aluminium wire m, n, supporting the gold leaves, passes down the
centre, and is held in position by the tube t, the joint between the glass
and aluminium wire being made vacuum-tight by filling the cup c with
" siegelwachs."

Two pieces of lead foil a, a, about $1\frac{1}{4}$ inches wide, are cemented on to the outside of the glass enclosure opposite the faces of the gold leaves, and are joined together by strips of lead foil x, y which completely encircle the glass enclosure.

A copper wire w is fastened over the strip of lead foil to allow a connection to the metallic coating to be easily made. The tube e is connected to a series of drying tubes, and to a pair of five-fall Sprengel pumps, to maintain a high degree of exhaustion in the enclosure.

With the instrument thus described, the following experiments were carried out, both while the electroscope was still connected to the pumps and after it was sealed off :—

Experiment 6.—A copper wire w was passed round the outside of the electroscope so as to connect together the two outside metallic coatings a, a. A fine wire v was then attached to this surrounding wire, and was connected to the aluminium wire m, n, from which the gold leaves are hung. Thus the *gold leaves are put in metallic connection with the outside coating* of the electroscope. A wire was also taken from the surrounding bands of lead foil x, y to the gas pipes, etc., and; thus all question was avoided as to the condition, as to insulation, of the gold leaves and the surrounding coatings, all the parts being put in metallic connection with each other, with the earth, and with the general surroundings.

It is to be remembered also, in this connection, that the outside of the glass enclosure of the electroscope *is not an insulator ;* it was not dried, nor specially cleaned, and no part of it could be charged to the smallest degree by means of rubbed glass or rubbed sealing wax. To test this, a second independent electroscope was charged, and when the knob was brought into contact with any part of the glass of the first, it was instantly discharged, and this was the case even when all the wires; described in the last paragraph, were cleared away.

With the arrangements which have just been described, it will readily be understood that if a rod of glass be rubbed with silk (vitreously electrified), or a rod of sealing wax with flannel (resinously electrified), and brought near to the electroscope, no effect is produced. The gold leaves, being connected to the outside of the cover and to " earth," and being protected by a conducting envelope, cannot be electrified in the ordinary way. This was verified by experiment.

Experiment 7.—In these circumstances, when the flame of a spirit lamp, or a light of any description, was suddenly brought up towards the electroscope, the leaves were instantly seen to diverge, and when the flame was withdrawn suddenly the leaves fell together again, but they did not

respond instantly, as in the case of the divergence. In this experiment the flame is not brought into contact with the glass; the effect is produced at a distance of many centimetres from it. The glass is not heated, or quite infinitesimally.

Experiment 8.—When the flame is suddenly brought up and then withdrawn, and this operation performed three or four times in succession, taking care never to heat the glass to the slightest degree, the gold leaves obtain a large permanent repulsion for each other, and stand permanently apart. The leaves could even be torn from their support by operating thus with the spirit flame, if care was not exercised to avoid such violent action.

By suitably manipulating the spirit flame, the gold leaves can be deflected in very curious ways. The flame being suddenly pushed up towards them, sometimes from one direction, sometimes from another, the leaves can be gradually contorted into a sort of crumpled form. They can both be driven in the same direction relatively to the centre; and they remain in this contorted condition, only slowly resuming their natural state.

It is difficult to make a drawing to illustrate the crooked forms into which the leaves are sometimes twisted, but an attempt to do this is made in figs. 4 and 5. This twisting makes it evident that the leaves are subjected to
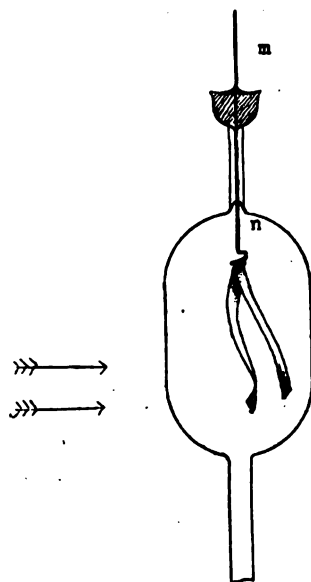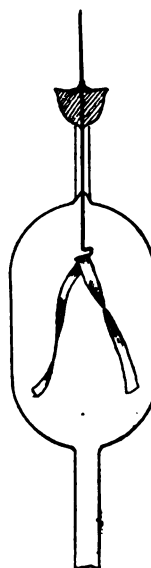
FIG. 4. FIG. 5.

considerable local forces, with rapid variations, as to direction and amount, from point to point within the enclosure. Putting the hand to the aluminium

wire *m*, *n*, or catching hold of it between the fingers, makes no difference to the gold leaves ; nor does the putting of a spirit flame (Gilbert's and Faraday's method of discharging electrification) in contact with the outside coil at the end of the aluminium wire *m*, *n* have any effect. The deflection remains unaltered, and the leaves are not relieved of their charge, as would be the case with an ordinary charged electroscope.

Experiment 9.—To find whether the gold leaves were affected from a distance by a source of light, a Nernst lamp was set up about 6 metres distant from the electroscope, and the image of the filament was projected upon the glass enclosure. As soon as the light from the Nernst lamp fell upon the gold leaves, they instantly diverged, although not to the extent of the divergence obtained in previous experiments, when the lower ends of the leaves were often 2 or more centimetres apart. When an opaque screen was interposed between the source of light and the electroscope the leaves quickly collapsed. If the screen was passed backwards and forwards across the path of the rays, the leaves alternately diverged and fell together again. Even the movements of the string of a pendulum swinging across the beam of light could be followed, by observing the slight kicks of the leaves, which were produced when the light was momentarily cut off by the string. Screens of glass, or other transparent substances, have practically no effect in cutting off the radiations which affect the gold leaves. The leaves responded to the movements of a shutter in front of the lamp when the light was made to pass through a plate glass door, just as if the door were not there.

Screens of various materials were interposed between the electroscope and the Nernst lamp. When the light was transmitted through coloured glasses the divergence of the leaves was diminished, ruby glass almost halving the deflection. The effective radiation appears to pass with the greatest freedom through several sheets of white, or coloured paper, so long as the screen is at all transparent to light. A parallel-sided plate of ice was made, by sawing a slice off a large block of ice and then rubbing its surfaces down on a sheet of plate glass, until they were quite parallel and true. The sheet of ice allowed the peculiar radiations which affect the gold leaves to pass through, with scarcely any perceptible diminution in intensity. No effect, however, could be detected when the Nernst lamp was replaced by a spirit flame, the sheet of ice still being present, although the light from a candle or match would produce the effects observed with the Nernst lamp. This was also found to be the case when another vacuum electroscope was completely immersed in a glass vessel of alum solution, and the Nernst lamp, and the various flames, brought near to the gold leaves. The Nernst

lamp,* and the flames of a candle or match, produce their full effect; but the influence of the spirit flame, as far as can be detected by visual observation of the gold leaves, is completely stopped. Screens of lead, copper, zinc, etc., appear to stop, or at any rate to reduce greatly, the radiations which affect the gold leaves. Some curious observations, however, which may modify this last statement, were made when the radium clock was the subject of experiment. It was found that metal screens allowed radiations to pass through, which repelled the gold leaves of the radium clock, and thus caused its period of charge and discharge to be lengthened. Tables showing this numerically will be given in a future communication.

Experiment 10.—It was found that divergence of the leaves only took place when the light was shining directly upon them, and that no effect was perceptible when the light was projected through the glass envelope, without illuminating the gold leaves. In testing this, the image of an incandescent electric lamp was focussed by means of a lens first upon the gold leaves and then upon the glass cover, the gold leaves being avoided. The result mentioned above was obtained, but it was also found that if only one leaf was illuminated the opposite leaf was repelled away from the illuminated one, which remained hanging vertically, as shown in fig. 6. If the spot of light was so arranged that it illuminated a little patch in the centre of one of the gold leaves, the opposite leaf took the form as shown in fig. 7, very different from any that could be due to electrification.

The gold leaves of the vacuum electroscope show a distinct deflection when bright daylight falls upon them, and a large divergence is obtained if the gold leaves are illuminated by direct sunlight. A black card interposed, so as to cut off the light, causes the leaves to collapse at once; but they again attain their maximum deflection the instant the card is removed.

Turning the electroscope round its own vertical axis, so that the rays of light, from the sun or any other source, may fall on the gold leaves at different angles, increases or diminishes the amount of the repulsion of the leaves.

Experiment 11.—To put in evidence further the difference between these phenomena and such as could arise from electrification of the vacuum electroscope, the following arrangements were made, of which fig. 8 is a diagram.

The gold leaves and metallic coating of the vacuum electroscope A were connected up to the corresponding gold leaves and metal plates of an

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* Care must be taken when the Nernst lamp is used as a source of light in these experiments. The metallic holder of the lamp is frequently electrified, and it ought to be "earthed" by means of a suitably connected wire. It also seems as if the Nernst filament were perpetually shedding off an emanation, which will electrify an ordinary electroscope placed at a distance of several inches from it. This electrification is *resinous.*
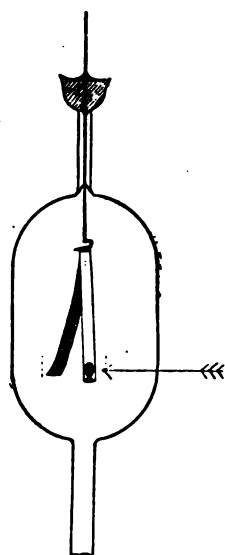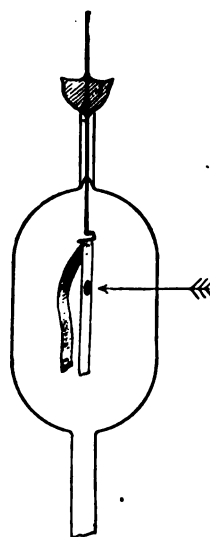
Fig. 6.   Fig. 7.

independent electroscope B.   A wire *p* made connection between the metallic
coatings and "earth."   The two electroscopes were exactly similar in con-
struction ; the main difference between them was that one had a high vacuum
and the other had no vacuum.   The gold leaves of both were of the same
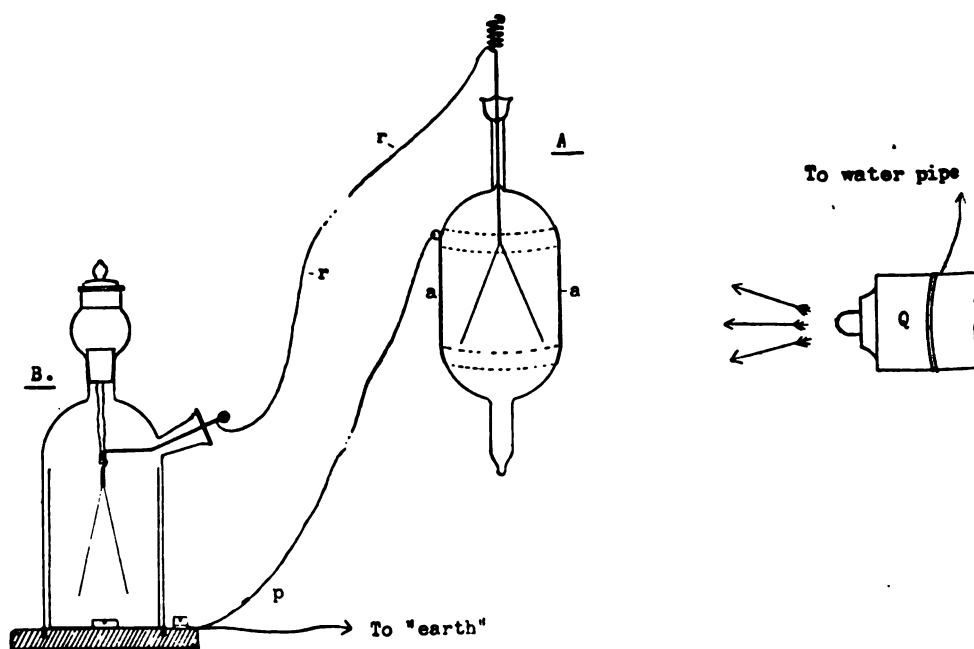
Fig. 8.

length and width, and the glass enclosures were made from the same piece of glass tubing; thus, if a common charge were given to the electroscopes, the lower ends of the gold leaves would stand apart at approximately the same distance in each. A Nernst lamp Q, with its metal cover connected to a water pipe, was brought near to the electroscope A; the gold leaves at once diverged, and those of electroscope B also diverged, but the distance apart of the leaves of B was not more than half the distance by which those of A stood apart. If now the wire *r* connecting together the gold leaves of A and B was touched with the hand, electroscope B was discharged, but electroscope A was only partially discharged.

When electrified rods of glass and sealing wax were brought up to electroscope B, the charge on the leaves was found to be *resinous*, but the charge left on the gold leaves of A, after the electroscope B had been discharged by touching the wire *r*, was not electricity at all. To confirm this, both electroscopes were charged "vitreously," and when the Nernst lamp was brought up to electroscope A, the "vitreous" charge of electroscope B was neutralised, but the gold leaves of A remained apart so long as the light from the Nernst lamp fell upon them. If a spirit flame was used instead of the Nernst lamp, no charge could be got on electroscope B, although the gold leaves of electroscope A stood wide apart.

Other vacuum electroscopes, having metallic coatings of fine brass wire gauze and aluminium foil on the *inside of the glass enclosure*, were set up, and all the foregoing experiments were repeated. The results obtained, although of smaller magnitude, correspond with those already described in connection with the electroscope with the metallic coating on the outside of the glass envelope.

The experiments described above are to be considered as preliminary. The phenomena are still under observation, and we hope in a future communication to be able to lay before the Royal Society further details with regard to the magnitude of the forces concerned, and the laws which govern their action.

Since the paper was communicated to the Royal Society, our attention has been called to a short paper by Sir William Crookes, of 1879, published in the 'Proceedings of the Royal Society,' in which certain movements of gold leaves in vacuum, similar to those which we have observed, are described.

Report of Private Expedition to Philippeville, Algeria, to view the Total Eclipse of the Sun, August 30, 1905.

By T. C. PORTER, M.A., D.Sc., F.R.A.S., etc., and W. P. COLFOX.

(Received November 27, 1906,—Read May 30, 1907.)

[PLATES 4 AND 5.]

General Objects:—

To examine—

(a) The height of the reflecting layers of the atmosphere.

(b) The structure of the corona.

(c) The polarisation of the corona.

(d) The coronium ring.

(e) The shadow bands.

(f) The meteorological conditions of the eclipse.

Our station was near Philippeville, about 1·5 kilometres to the west-north-west of the village of Saint Charles, on the long and broad summit of a grassy hill rising at a moderately steep slope. The position of our camp, as given by the large-scale survey map, was:—

N. Lat., 36° 45' 38"·7.

E. Long., 6° 51' 59"·1, or in time, 0 h. 27 m. 27·6 s.

Height above sea-level, 690 feet or 210 metres.

These values agreed well with independent observations made with sextant and telescope.

A space on the north side of the hill, and about 5 feet below the highest plane, immediately under and to the north of a thick bushy tree, about 16 feet high, was cleared of grass and levelled by Arabs. On this we set up a double-roofed tent, and were thus greatly protected from the sun during the heat of the day.

The circumstances of the eclipse for our position, which was almost exactly on the line of central eclipse, are given in the following table; the time, unless otherwise stated, being our *Camp mean time.*

The second contact was observed with a field glass, one objective of which had a direct-vision prism before it. The third was observed with the same apparatus as the second, but a "coronium green" screen was placed before the otherwise bare objective, a plan which the observer thinks is to be strongly recommended. The fourth contact was observed through the 4-inch telescope, with a power of 120, and suitable screen.

Contact.	Calculated from N. A.	Observed.	Possible error, if + to be added to the mean time.	Position angle.	Angle between N. Pt. and vertex.
	h. m. s.	h. m. s.	s.	° ′	° ′
1st	0 40 9·9	—	—	295 43	16 21
2nd	2 0 10·0	1 59 58	−6	115 21	} 39 48
3rd	2 3 47·2	2 3 34	+1	293 39	
4th	3 16 59·6	3 16 46	−1	114 54	50 0

As the position of our camp was isolated, we depended upon our own observations for the time, and also for the determination of the watch's rate error. The watch was a half-chronometer by " Longines " 1201182 ; it lost 1·8 secs. per hour, and the resulting errors in times of observation have been allowed for in the above table. To find the time, we used the method of equal altitudes, making the observations with the sextant and artificial horizon.

The seconds during totality were given by a metronome, and the duration of totality by using a stop-watch from second to third contact.

The apparent diameter of the sun at the observing station was

$$0° 31' 44''·73.$$

The apparent diameter of the moon at the observing station was

$$0° 33' 15''·18.$$

Apparatus.—This was of so simple a nature that it may be very shortly described :—

(1) A 4-inch clear altazimuth telescope of 5 feet 4 inches focal length, by Dollond, of excellent performance. It had no driving clock, slow motion in R.A. and Decl. being given by two handles worked by the observer. Originally it was intended to use this telescope for photographic purposes, and a special circular plate carrier was designed and made for the purpose, but it was found that the vibration was too great, even with rapid exposures, and so the instrument was used visually.

(2) A brass-bound stereoscopic camera, with Zeiss anastigmat lenses of 6·5-inch focus, each lens having in front of it a large Nicol prism. The camera and Nicols were mounted together on one stand, all being adjustable in altitude. This was placed in position the day before the eclipse, and focussed with a special high-power lens by Dallmeyer. For the stand, and for that mentioned in (3), our thanks are due to Mr. R. W. Kennedy.

(3) A 14-inch by 10-inch camera, with a Dallmeyer's R.R. lens of 16·5-inch

focal length, used at aperture f/8·5, and covered with a special green screen, described later, supplied by Messrs. Sanger Sheppard and Co., for the purpose of transmitting green coronium light and little else.

(4) A quarter-plate and half-plate camera, each with its stand, also standard thermometers, a fine aneroid barometer by Browning, sextant, artificial horizon, and other accessories.

(5) A portable dark tent, with table, which was used solely for placing the plates in the holders the night before the eclipse. The plates used were specially made by Messrs. Cadett; they were sensitised for the whole spectrum, very well backed, packed in tins, the cover of each tin being held in position by a strip of surgeon's plaster. Although these plates went through all sorts of temperatures from 12° up to 40° C., they showed no trace of deterioration, though they were not developed for more than two months after exposure. Development took place in total darkness for the most part.

General Observations during the Eclipse.—From a few minutes after first contact, the progress of the eclipse was watched through the 4-inch; and the times (St. Charles mean time) of the disappearance, and, after totality, the times of reappearance, of the four groups of sun-spots visible were carefully noted as follows :—

	h. m. s.	h. m. s.	h. m. s.	h. m. s.
Disappearance	1 17 4	1 43 44	1 52 34	1 56 36
Reappearance	2 37 44	3 1 4	3 5 14	3 12 54
Small train of spots uncovered at	3 2 44			

From the rate of the moon's motion and the path of its centre across the sun, the apparent positions of the spots (within 23 secs.) on the sun's disc have been calculated, and are indicated in fig. 1, which also gives the circumstances of the eclipse as seen from our camping place.

Some interest attaches to these spots, especially to (c) and (d), notably (d), which lay close to the limb. The great north-east prominence—such a noticeable feature of this eclipse—was situated, as the figure shows, just above the region of these spots.

At 1 h. 42 m. an observation of the amount of atmospheric "flare" round the sun showed that it was considerable; it could be traced fully 8° from the sun's limb; the observer, who has made a special study of this flare in many latitudes and at various altitudes, considered, from the character of the flare, that in all probability the particles causing it were not at any very great altitude, nor in a layer of great thickness. The distant hills, quite 30 miles off, were beautifully clear, so that the stratum of dust seemed certainly above us.
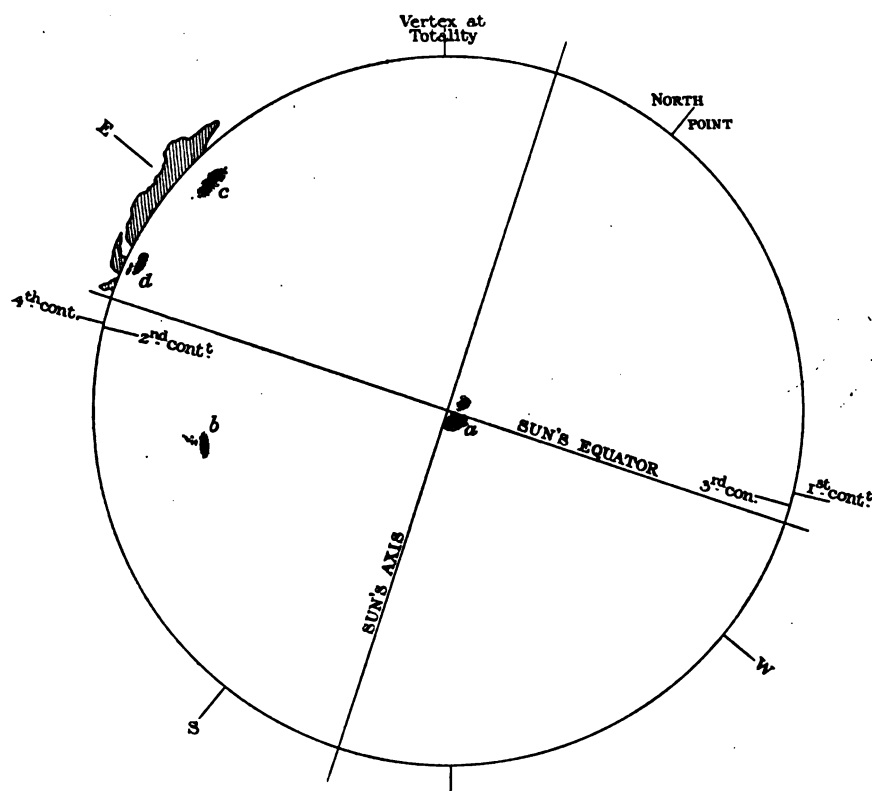
Fig. 1.

Taking 5° as the upper limit of the brilliant orange glow seen above the south-west horizon, at from 6 to 9 secs. after central totality, we find, for the *upper* limit of the stratum of reflecting matter in the atmosphere, almost exactly 6 miles, a result coming near the inferior limit given by a very large number (many hundreds) of observations made by the present writer during many years in different latitudes at sunrise and sunset. If h be the required height, A the altitude of the orange glow, P the position of the observer, O the centre of the earth, Q the observed greatest altitude of the glow, and B the angle POQ, then from fig. 2 given below it is easily seen that $(h + r)/r = \cos A/\cos (A + B)$, which at once gives h.

Photographs and Visual Observations of the Corona.

(*a*) Unassisted visual observations : A drawing, on a previously prepared scale, was made by W. P. C., who possesses very keen sight, of the three most prominent coronal streamers. The observer had carefully abstained from looking at the solar crescent for some little time before totality, but had not

closed his eyes, as he was busily engaged in observing the shadow-bands. Of the two streamers near the south pole of the sun, the more remote he could trace with certainty for 2·0 moon's diameters, *i.e.*, 1° 6' 30"; whilst that nearer to the pole certainly extended one-tenth of the diameter further, *i.e.*, 1° 9' 30". The third streamer, which lay in the north-west quadrant, extended visibly not quite 1·5 lunar diameters from the limb, or 0° 50'. No screen was used to hide the inner corona from the eye.
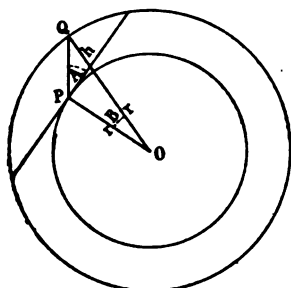
Fig. 2.

(*b*) Two photographs of the corona were taken simultaneously through two Nicols inclined at 45° and 135° respectively to the horizontal, and exposed from the 40th to the 45th second after second contact. (See Plate 4, figs. 3 (*a*) and 3 (*b*).)

The effective apertures of the two Nicols were 2 inches and 2·5 inches respectively, and to make the two photographs strictly comparable the aperture of the lens behind the larger Nicol was stopped down till the two images on the ground glass of moderately bright objects seemed, after careful estimation, to be of the same degree of brightness. (This adjustment was very carefully made on August 29.) The plane of polarisation of the atmosphere was roughly ascertained, before the exposure was made, by a rapid survey of the sky with a small Nicol; it was nearly, if not quite, horizontal, so that the atmospheric polarisation affects both the photographs sensibly equally. A glance at the result, figs. 3 (*a*) and 3 (*b*), is sufficient to reveal the fact that the light of the outer corona is powerfully and radially polarised. The longer of the two southern streamers on the left-hand negative can be traced with certainty for 2·2 diameters (0·2 diameter further than the visual estimate) away from the moon, and with equal certainty to within 2' 7" of the moon's limb, yet no part of this streamer can be traced with certainty on the negative from which the right-hand print has been made; its light seems, therefore, to be polarised throughout the greater part of its length, and the same thing is true, so far as one can judge from the photographs, of the other streamers. So far as these prints and the negatives from which they are made are concerned, there seems to be unmistakable evidence that either the general brightness, or the extent, or the amount of unpolarised light, or all three, were greater on the north-east side of the sun than on any other side; that is on the side where the great prominence was visible. This can be seen on *both* the simultaneous photographs.

The curved lines of the plume of coronal streamers to the north and south of the great prominence have their convex sides towards the prominence, so
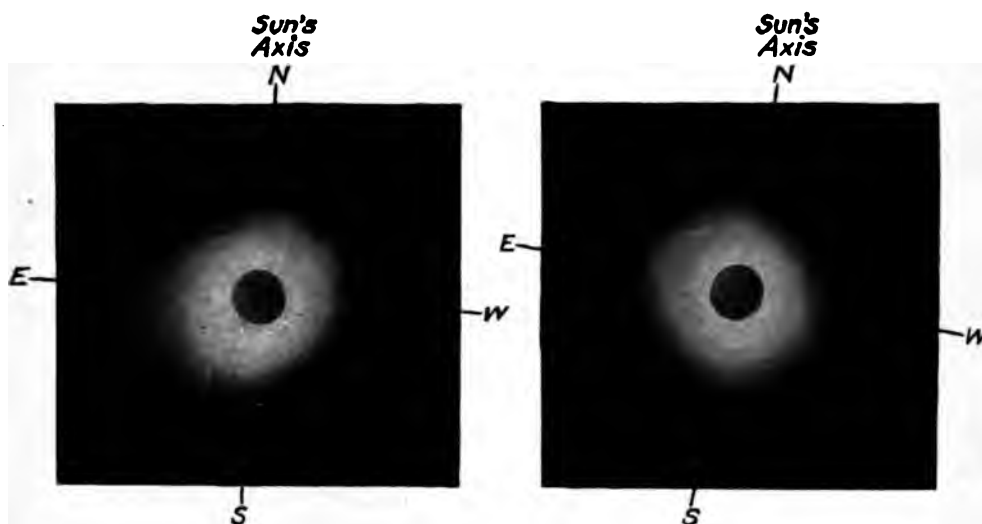
FIG. 3 (*a*).
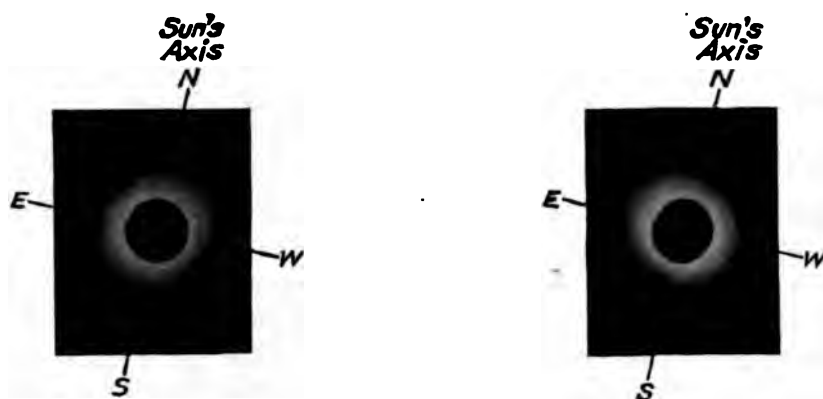
FIG. 3 (*b*).
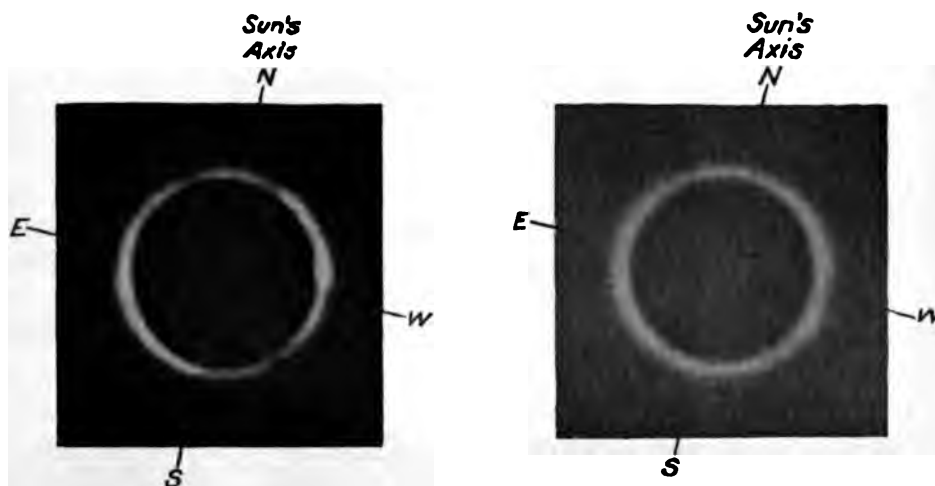
FIG. 4.

far as we can see, and suggest that even if their cause is independent of the cause of the prominence, yet that the latter has some disturbing influence upon their direction.

Our thanks are specially due to Messrs. Harvey and Peak, of Charing Cross Road, for their great kindness in lending us freely the larger of the two Nicols, without which this part of our work must have been impossible.

(*c*) Visual observations of the *inner* part of the corona with the 4-inch refractor, using the reflecting solar eye-piece, and a light, neutral tinted shade, on the eastern and western equatorial regions of the sun, with a power of 120 diameters, during the last 90 secs. of totality.

(1) *On the Eastern Region, about the Point of Second Contact, along an Arc of about* 35°.—At first the field of view seemed filled with very pale cream tinted light. After three seconds of gazing the detail began to appear, first the broader streamers, and then the finer markings. This gradual appearance was, no doubt, due to purely physiological causes. This part of the corona was exceedingly intricate in structure. From the dark limb of the moon, which in its advance had already completely covered the big prominence, thin, straight, radial streams of pearly white luminous matter stood crowded together, like thin pillars of stalactite in some limestone cavern, or the trunks of young pines in a thick wood. Not far from the limb, these seemed to unite by each one widening at the top, forming what resembled a thin shell of white haze, but the observer failed to note how far this shell extended along the limb. It may have been confined to some 9° to 12°. As to the angular height of the thin pillars, memory would place it at 0° 1′ 40″, and the thickness of the "ceiling" at 10″, but neither dimension was recorded at the time. It is certain, however, that part of this structure lay above part, if not all, of the big prominence (which was, as has been said, invisible). It is also certain that it was crossed obliquely by a few streamers, which were three or four times wider than the pillars, and cut their direction obliquely. One streamer was particularly easy to see. It was curved, with its concave side towards the sun, and made, at the moon's limb, an angle of *apparently* 60° with the radial direction, sloping away from the limb towards the solar south. This columnar structure could scarcely be an upheaved part of the photosphere,* for it lay above the upper limit of the great prominence, and its light was of a different order to the photospheric. It may have been due to eruptive matter, reduced to a linear form by threading the spaces between the condensed matter which forms the faculæ. If, then, some of the constituents of these columns condense, these may form the luminous "ceiling" described, which will act as a reversing layer to the light of these

* *Vide* Mr. J. Evershed, 'Report, Eclipse Exped. Pineda de la Sierra, Spain,' p. 55.

components of the columns, whilst the uncondensed material passes on.
When, during later condensation, its particles attain the right size, they will
be driven away from the sun by light-pressure, forming the corona.

(2) *Telescopic Observations on the Western Equatorial Region.*—Nothing
of the kind seen in (1) was visible, but it is just possible it may have
been overlooked. The faint, softly defined, yet distinct outlines of the
streamers seemed to cross one another at all sorts of angles; but before any
rough quantitative measurements could be made, a number of luminous jets
were gradually uncovered by the dark limb, giving to the latter a serrated
appearance. These jets were exceedingly beautiful. They had very narrow,
sharply defined, brilliant white, or greenish white stems (next the sun) and
these stems rapidly widened into pear, or crocus-bud shaped heads, their
colour passing by insensible gradations from the glowing white of the stems
into rounded soft looking summits of the bluish-pink of the cyanogen flame.
They nowhere resembled the crimson of the hydrogen " vacuum " tube.
Some 10 of these were visible in an arc of the moon's limb subtending about
40° at the centre. They seemed perfectly stationary. The dark limb of the
moon was quite steady and sharply defined, in fact the " seeing " throughout
totality was unusually good. There is no doubt in the observer's mind that
some of the inner coronal streamers could be traced down to the upper limit
of these brilliant jets, which he supposes were part of the chromosphere.

(*d*) On the photograph of the " coronium ring ": This was taken at central
totality, with the lens and camera described under Apparatus, heading (3),
with 5 secs. exposure, f/8·5, with the green screen. The result is shown in
the two prints from the intensified enlargement (fig. 4). The lighter of the
two prints shows the utmost extent of the radiation, which corresponds to
some 123,000 miles above the photosphere in the places where it is highest,
and 61,000 miles where it is lowest. The darker of the two prints is from
the same negative, and is intended to show the detail present in the ring.
Not less than 40 glowing points or jets can be counted on the negative, and
their distribution does not show any obvious relation either to the ordinary
prominences nor yet to the coronal streamers. They seem to be a phenomenon
per se. To find what radiations the screen used would have allowed to pass
had they been present, four photographs of the ordinary solar spectrum were
taken with direct sunshine through the screen, on the same kind of plate as
was used in the eclipse and, moreover, one of the same dozen. The shortest
exposure, 5 secs., shows a faint band with limits of wave-length at 5181 and
5577, and with maximum at 5508.

It might well be suggested that these jets were not of coronium, but of
some matter giving a continuous spectrum ; if so, they might be expected to

show on other photographs, not taken through a green screen, and they do not; but this may be answered by saying that their light is swamped when *all* the light of the inner corona is allowed to fall on the photographic plate. If we set aside this explanation and search among elements known to exist in the upper chromosphere or in the corona, by strong lines within the range of the spectrum transmitted by the screen, 5181—5577, then the choice seems to be limited to—

(1) Magnesium, " *b* " lines: impossible with the exposure given, and evidence from Guelma that the Mg lines faded out before central totality.
(2) Coronium, 5303.
(3) Helium or hydrogen: practically out of court, from the nature of the light transmitted by the screen, and also much evidence to prove that the coronal material is independent of the H and He of prominences.
(4) Iron enhanced lines, 5169, 5316, 5363, and 5535: all most unlikely, from their faintness and from the elevation of the " coronium ring."
(5) Unknown element, 5425: if the detail is due to this, it should have been noticed in the corresponding ring of the slitless spectrographs made at Guelma, and this is apparently not the case.

Thus the bright points are almost certainly due to coronium.

Observations of the Shadow Bands.—These were particularly well seen, both before and after totality. In order to observe them, a white sheet, about 12 feet by 9 feet, was carefully orientated and stretched on level ground. Several staves of white wood, 2 metres long and 2 cm. wide, some marked and some plain, were used to determine the direction of the length of the shadow bands, both before and after totality. About 4 minutes before totality one could see that " something" was passing over the sheet. Gradually the bands grew more distinct, and were plainest about 2 minutes before second contact. The observer could not feel certain whether they disappeared before totality; they certainly grew more indistinct. Before totality, the breadth of the dark part of each band was about 0·5 inch, after totality they were certainly thicker—about 1 inch—and not only more distinct, but more distinctly waved. The distance between the bands was the same, both before and after totality, namely 4 inches, with a possible error of ±1 inch. After totality, they remained visible for 3 m. 30 s., the time of their disappearance being well observed. When most distinct, the bands were dark grey in the middle of their breadth, but shaded off gradually but quickly at the edges. They were not coloured. The rate at which they travelled, measured at right angles

to their length, was estimated at from 6 to 7 miles an hour. They were scarcely, if at all, visible on surrounding objects, and it seems clear that to observe them successfully, a smooth, white surface must be used. An attempt to photograph them before totality failed. A second sheet was stretched over some low bushes in front of a camera, but, unfortunately, it was not sufficiently secured and became creased, when too late to remedy the fault.

The direction of the bands themselves before totality was from 38° east of north to 38° west of south, and was the same within the errors of experiment after totality. As a matter of fact, the after-totality stick made an angle of 0° 22′ with the before-totality stick, lying nearer the north and south line by these 22′.

These directions coincide, within half a degree, with the trace on the horizontal sheet (on which the bands were observed) *of the plane passing through the cusps of the solar crescent and the sheet.* Being almost exactly on the line of central totality, the angle through which the trace of the cusp line rotated during totality was very small, but, so far as the observation went, the bands rotated with it. This is the first time, the writers believe, that such evidence has been adduced. It accounts completely for the rotation of the direction of the bands' length noticed in many instances where the observers were *off* the central line, and explains why sometimes the bands are not seen ; for if the lines of differently refractive material in the air are not nearly parallel to the cusp line, it is obvious that no shadows will be cast. This last statement has since been proved by direct experiment with an artificial eclipse. The true direction in which the bands travel has *never* yet been determined ; they *appear* to move at right angles to their length, but this must *always* be the case with endless lines which have no distinguishing marks upon them. In the present instance the ripples on the bands, viewed "end on," seemed to have an independent motion along the bands from south-west to north-east, and this makes it certain that the *true* direction of travel of the bands was *not* at right angles to their length: nevertheless, if the eye fixed on any particular wave, it seemed, viewed from most positions, whilst it lasted, to move "straight forwards." The velocity of the ripples along the bands would, therefore, appear to be small when compared with the velocity of the bands themselves.

Meteorological Data of the Eclipse.

General Statement.—(a) Barometric observations, made with an open-scale aneroid by Browning, which has been used for many years, and is thoroughly known by one of the observers. The instrument has been proved to be well compensated for temperature ; its errors have been determined from time to

time by comparison, over a *narrow* range only, with a standard Fortin, under *naturally* (and therefore slowly) varying conditions of temperature and pressure and found to be at least as reliable as the best instruments of its class. It could be read correctly to 0·02 of an inch (0·7 mm.).

In making the meteorological chart, Plate 5, the readings have all been reduced to 0° C. and sea-level for the sake of comparison.

Note.—Owing to a mistake in the first estimate of the height above sea-level of the observing station, all the barometrical readings on the curve are 1·7 mm. too low.

(*b*) Thermometric observations: (1) The air temperature, read from a standard mercury thermometer (°F.), in the shade, about 4 feet from the ground. The readings are reliable to 0°·1 C.

(2) A standard "black bulb *in vacuo*" solar radiation thermometer, *un*shielded, and therefore showing, in addition to the solar, the radiation from the sky, and surrounding objects. This was fastened to the telescope stand in a fixed position, so that the sunshine fell on the bulb uninterruptedly from sunrise to sunset. The readings are accurate to 0°·1 C.

In the curves on Plate 5, no allowance has been made for this lag of the instrument in giving its indication, but on the *separate* radiation time curve, fig. 5, such an allowance has been made, based on the results of a direct comparison of the instrument's indications with those of a thermo-
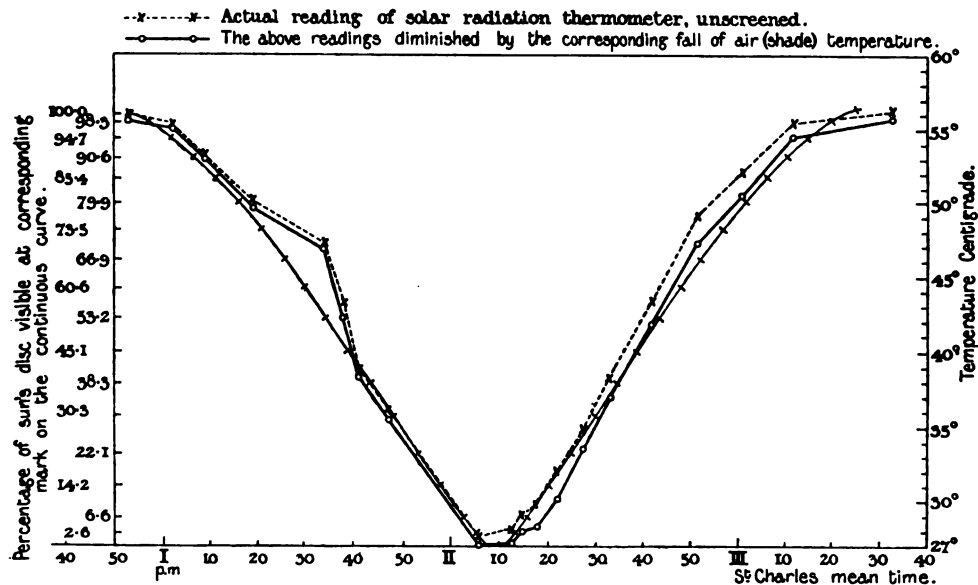
Fig 5.

pile, during an artificial "heat" eclipse, made roughly to imitate the real. The indications during the first and last part of the covering and uncovering of the sun's disc seem to have been approximately 8 minutes late.

(*c*) Measurement of the relative humidity of the air. The dry and wet bulb method was followed with the usual precautions. The apparatus was placed about 4 feet above the ground, the thermometers shielded from all but "light airs," and kept always in the shade. In every case the relative humidity has been derived from the readings by means of the formula—

$$\text{Relative humidity} = \frac{T_{w.b.} - a\,(T_{d.b.} - T_{w.b.})}{T_{d.b.}} \times 100,$$

where

$T_{w.b.}$ = Tension of aqueous vapour at wet bulb temperature,

and

$T_{d.b.}$ =   „   „   dry   „

whilst "*a*" is a factor depending on the barometric height, and having a value between 0·6056 and 0·6035 in these reductions.

It will be seen on the chart that two curves are given for each of the quantities observed, *i.e.*, the mean curve, and that for August 30, the day of the eclipse. Since the observations were limited to four days in all, it would be wrong to attach any great importance to the mean observations, were it not that one day very closely resembled another, and also that, as far as we could learn, the weather was of the usual kind for the end of August.

(*d*) Observations of wind were regularly kept. On the chart, the wind's direction, force, and character are given for every hour of the day from 5 A.M. till 6 P.M. As usual, the lengths of the arrows denote the force, each division of the chart-scale corresponding to ten units on the ordinary scale of wind-force: thus the strongest winds shown mean strong breezes of force 4. The arrow points *with* the wind, *i.e.*, to the quarter towards which the wind was blowing at the time indicated. If the arrow's stem is straight, it implies a steady wind; if wavy, a gusty wind. Where two or more arrows are drawn diverging from the same point, it signifies that at the corresponding time the wind was uncertain, blowing from either direction alternately, and changing through the acute angle between the arrows. A small circle with an arrow head on it means that the wind was shifting all round the compass in the direction towards which the arrow-head points.

(*e*) Observations of cloud. These are also given for every hour of the day — by small circles representing the whole visible sky, in plan, orientated as usual marked, and the *kind* of clouds, as well as their positions, are indicated by the method explained on the chart itself.

No attempt has been made to *smooth* any of the curves, but the

jaggedness is not to be attributed to errors of observation, *e.g.*, the minor peaks on the sides of the eclipse barometric " hillock " undoubtedly correspond to real subsidiary barometric fluctuations; that this is so is almost evident from the chart itself, for corresponding fluctuations are clearly traceable, both in the direction and force of the wind and in the humidity curve. The correspondence between the barometric and the humidity curves is remarkable ; almost every small peak on the former has a simultaneous variation—a rise and fall—or, more correctly, an increase and decrease in the rate of rise, or a decrease and increase in the rate of fall—on the humidity curve.

The question may be asked—How much, if any, of the " depression " in which the eclipse hillock lies is due to the eclipse ? The eclipse began on the earth at 10.30 A.M., G.M.T., in Labrador, ended for the earth generally, off East Africa, at 3.37 P.M., G.M.T., *i.e.*, at 4.7 P.M., St. Charles time. It seems therefore, that the big depression is *not* due to the eclipse, at all events mainly, and we must therefore consider that the first certain effect of the eclipse on the barometer is the pronounced upward turn at 0.30 noon, and that the eclipse ceased to have any *certain* effect at 3.36 P.M.

At 0 h. 30 m., the edge of the *penumbra* was approximately 283 miles away, at a point 60 miles south of Palma. At 3 h. 34 m., the edge of the *penumbra* was 481 miles away, approximately, *i.e.* about 40 miles due east of Tripoli.

The total length of the certainly disturbed barometer district, at any one moment, was, therefore, some 5000 odd miles, the part of it preceding the centre of the *umbra* being some 200 miles shorter than that following it, the isobars being closer together on the advancing front of the disturbance than in its rear. The most rapid barometric rise took place between 1.0 P.M. and 1.45 P.M., whilst the central portion of the sun's disc was being covered. The barometric maximum seems to have travelled some 500 miles behind the centre of the *umbra*, and seems to have covered a region about the same number of miles in length, measured along the line of central totality.

On the Eclipse Wind.—The general effect of the eclipse on the wind was two-fold : First to diminish its intensity, the minimum velocity of the wind occurring (unlike the barometric maximum) during totality, when it sank almost, if not quite, to zero,—and secondly, to make its direction before totality more easterly, and after totality more westerly, than in all probability it would otherwise have been, the influence after totality being the more plainly shown. Both are almost certainly due to the inrush of air from all sides towards the centre of the shadow, where the cooling and consequent contraction of the air were a maximum. Our station was on the central line, and the path of the moon's shadow was roughly from W.N.W. to E.S.E., and

if it be assumed that the influx of air took place fairly symmetrically, the wind *due to the eclipse* before totality must have been on the whole east-south-easterly, and after totality west-north-westerly, because the *components* of the wind's directions blowing in from opposite sides of the shadow track, *at right angles to that track*, must have neutralised each other, leaving only their east-south-easterly components active before totality, and their west-north-westerly components active after totality.

The actual wind observed was due to the superposition of this eclipse wind proper on the northerly sea breeze, which, though diminished considerably during the middle period of the eclipse, was throughout sufficiently strong to cause the wind to preserve on the whole a more or less northerly direction. It will be remembered that the direction of motion of the shadow bands, though not measured satisfactorily, had, in all probability, a large northerly component, and it is certain that their movement was *towards* the line of central eclipse. The region of higher pressure in the eclipse seems to be an exception to ordinary high-pressure areas in that the air flows *towards* the former, whilst it flows away *from* the latter.

On the Relation between the Solar Radiation, as measured by the unscreened Black-bulb-in-vacuo Thermometer and the uneclipsed Area of the Sun's Disc.— This is shown by the three curves in fig. 5 (p. 305):—

(*a*) The continuous black-lined curve shows the fraction of the sun's disc uncovered at any given time during the eclipse, but to get the true time corresponding to a given area from the diagram, it is necessary to subtract 8 m. from the time indicated, *e.g.*, at 1 h. 26 m. on the diagram, 66·9 per cent. of the sun's disc was visible, that is at true mean time, St. Charles, 1 h. 18 m. In this curve the variation of the rate of the moon's motion during the eclipse has been allowed for.

(*b*) The broken line curve of the black-bulb thermometer at the corresponding time indicated in the diagram.

(*c*) The curve with small circles on it, which lies everywhere below the broken line, gives the same temperature as the latter, diminished by the fall of the air shade temperature at the particular time considered.

The times as read in the diagram for (*b*) and (*c*) are approximately 8 m. too late: this is due to the lag of the thermometer.

To illustrate the use of the curve:—Take the indicated time 1.30, or in reality, allowing for the lag of the instrument, 1 h. 22 m. If the temperature had fallen in proportion to the area of the sun's disc covered, the temperature indicated by the thermometer would have been 44°·5 C.; instead of this the temperature shown by the radiation thermometer was 48°·3 C. (or 47°·7 if the fall in the air shade temperature be subtracted from it).

At the true time, 2 h. 40 m., when the same fraction of the sun's disc was uncovered during the latter part of the eclipse, the temperature, if proportional to the fraction of the solar disc showing, would have been again 44°·5 C. The temperature actually shown by the radiation thermo-meter was 47° C., and this, minus the fall of the air temperature, is given by the appropriate curve as 45°·4 C.

The general form of the radiation curve fits well with that of the areas uncovered, and the effect of the different radiative power of the margin and centre of the sun's disc is traceable. The bulge on the descending part of the curve is due in all probability to a terrestrial cause, as there is no corresponding bulge on the ascending branch—perhaps the temporary removal of some invisible screen of water vapour between 1 h. 12 m. and 1 h. 26 m.; if reference be made to the cloud chart, Plate 5, it will be seen, curiously enough, that it was during this very time that the only clouds from dawn till 5 P.M., on August 30, *appeared.* The record says: " 1.19, some cirrus forming between N.N.W. and W.S.W. . . . ; 1.24 the same, no bigger . . . ; 1.34, clouds in N.W. going . . . ; 1.41, clouds gone." Probably this is but a coincidence, but it is sufficient to show that there were layers of moist air at cirrus heights at the time, and the drifting past the sun of a gap in one of these would amply explain the bulge on the curve.

Stars Visible during Totality.—Several Arabs who stood on the hill during the eclipse kindly consented to keep watch for stars and planets; after the eclipse they pointed out the positions of six stars seen, without optical aid. They were identified as Venus, Mercury, Regulus, Spica, Arcturus, Procyon.

Before closing this paper we wish to give our most hearty thanks to all who helped in any way to make our expedition a success. First, and most of all, to Herbert A. Scratchley, Esq., M.V.O., His Majesty's Consul for Philippeville, without whose great experience and ready advice we should probably never have been able to get into our comfortable quarters in time for the eclipse. He spared no personal trouble for some days to help us in the choice of a site for our camp, and to him we are not only indebted for unvarying kindness and courtesy, but for introductions which proved exceedingly valuable, notably to Monsieur Emile Œttly, Mayor of St. Charles, who procured for us the loan of the school room as a temporary resting place for our apparatus; he it was who engaged Belouahem Mohamed, Arab Garde Champêtre, the man personally responsible for our safety, welfare, and the security of our luggage. M. Œttly also most kindly acted the part of Paymaster, and helped us in a hundred other ways.

We also owe a debt of gratitude to the Deputy-Mayor, M. Jean Roggy

to M. Pierre Chazerans, Secretary to the Mayor; to M. Jean Gaulin, Garde Champêtre; to Madame V$^{re.}$ Sogorb, whose excellent *cuisine* contributed no little to our health and happiness; to our two Arab Guards; and, lastly, to the courtesy of the French Government, which allowed our instruments and personal effects free entry into Algeria.

Chemical Reaction between Salts in the Solid State.

By EDGAR PHILIP PERMAN.

It has long been known that in a mixture of solid salts chemical reaction may take place. Experiments on the subject have been made by Spring (*vide infra*), Thorpe,[*] and others. My attention was first called to the question by observing that a mixture of arsenious oxide and cadmium nitrate underwent a slow but complete change of composition, the final result being that the nitric acid was eliminated, arsenic acid taking its place.

Preliminary Experiments.—Some experiments were made in order to discover what salts would be suitable for a careful investigation. The following were selected for trial, since a chemical change could be traced by an accompanying change of colour. The salts were finely powdered, but not specially dried.

Salts.	Result on mixing.
Lead nitrate and potassium iodide	Immediate action.
Lead chloride „	„ „
Lead formate „	Slow action.
Lead sulphate „	Very slow action, colour appearing after 30 minutes.
Lead oxide (litharge) „	No appreciable action.
Lead carbonate „	No change.
Mercuric chloride „	Immediate action.
Mercuric cyanide „	No action.
Mercuric chloride and potassium chromate......	Slow change.

From these salts two pairs were chosen for further study, viz., lead chloride and potassium iodide, and mercuric chloride and potassium iodide.

The salts were purified by recrystallisation, dried over sulphuric acid,

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[*] B. A. Report, 1881, p. 580.

ground in a mortar, and sifted through fine silk cloth, such as is used for sifting flour; they were then kept in desiccators over sulphuric acid.

Lead Chloride and Potassium Iodide.

Effect of Drying over Sulphuric Acid.—Equivalent quantities of the salts (2 grammes potassium iodide and 1·68 grammes lead chloride) were placed in two flasks, A and B (fig. 1), C containing concentrated sulphuric acid. The salts were occasionally warmed and shaken in order to make the drying more efficient. After standing 48 hours, the lead chloride was shaken from A into B, C being held in a horizontal position. The salts were mixed by shaking, when there was no apparent change of colour. The flask B, which had previously been drawn out, was then sealed off.
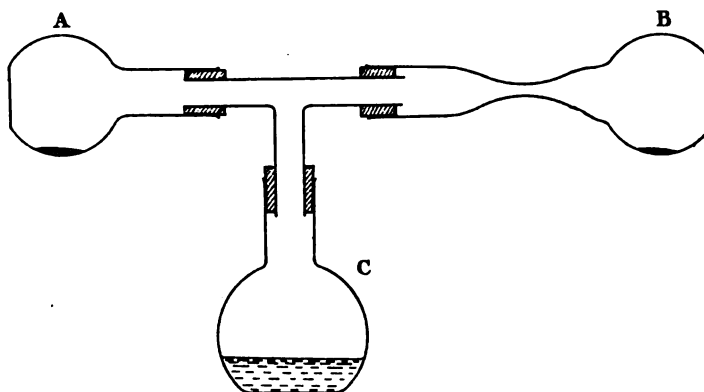
FIG. 1.

The mixture was watched from day to day; no change could be seen until the tenth day after mixing, when a very faint yellow colour appeared. On further keeping, the colour slowly deepened for some weeks, and then seemed to remain unaltered. In this experiment the mixture was kept in the dark.

Effect of Light.—Another mixture made in the same way, but exposed to daylight, behaved in no way differently from the first.

Effect of Temperature.—On heating a similar mixture at 100° for five hours, no colour appeared, but, on keeping, it showed a tinge of yellow at the beginning of the third day, showing that the reaction had been much accelerated.

Attempt to Determine the Minimum Quantity of Water Necessary to Produce an Immediate Visible Reaction.

Several methods were tried :—

(1) The mixture having been made in the usual way, the flask containing

it was weighed and allowed to stand open to the air on the balance pan until the yellow colour was perceptible. The increase in weight was then noted.

(2) The flask containing the mixture was connected, by a ground glass joint and wide stop-cock, with a small bulb containing crystallised borax. As soon as the yellow colour appeared, the bulb was detached, and the loss in weight of the borax determined.

(3) The substances were dried over phosphorus pentoxide, and mixed in an exhausted globe. Measured volumes of air saturated with water vapour were then admitted until the first appearance of colour. The weight of water admitted was calculated.

The results obtained by these three methods were not very concordant, the quantity of water varying from 0·1 milligramme to 1 milligramme. The smallest number is probably the most correct. The chief interest of the matter is in its comparison with the case of mercuric chloride and potassium iodide.

Mercuric Chloride and Potassium Iodide.

Owing to the volatility of mercuric chloride, it was necessary to dry the salts separately, for otherwise some of the mercuric salt was driven over into contact with the potassium iodide. Several arrangements were used ; in one a wide tube was divided by a glass septum, which was broken, after the salts were dried, by a glass rod enclosed. In another arrangement the separation was effected by a septum of fusible alloy, which was melted before mixing the salts.

The simplest device, however, was the following : Some potassium iodide was placed in a small thin-walled bulb and dried by gentle heating and at the same time exhausting with a mercury pump. The bulb was placed inside a wide tube closed at one end and containing some mercuric chloride; the other end was drawn out and the tube and contents were dried in the same way as the potassium iodide. The tube was then sealed off, and the salts were mixed by breaking the bulb.

As the result of these experiments, it was found that on mixing the salts a faint colour usually appeared at once. It was at first yellow, and changed, slowly or quickly, according to the thoroughness of the drying, into the scarlet mercuric iodide. If the phosphorus pentoxide (in the pump) was of poor quality or had been much used, the red colour appeared immediately on mixing the salts, but otherwise three days were required for the full development of the colour.

With specially made phosphorus pentoxide, more complete drying was obtained and there was no reaction. The arrangement used is shown in

fig. 2; A is the alloy septum. After introducing the salts B, B′, the tube was narrowed at C, C′. The phosphorus pentoxide was then placed at D, D′, and the tube sealed off at both ends. Next, the phosphorus pentoxide bulbs
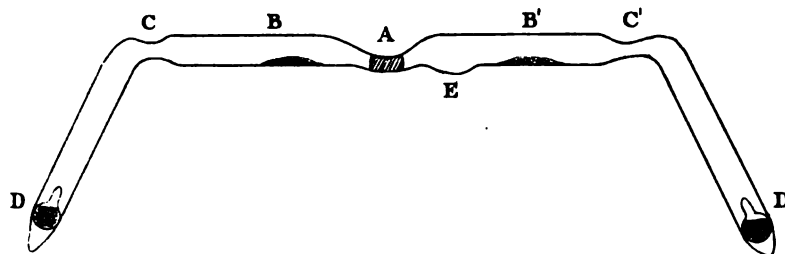
Fig. 2.

were broken and the whole allowed to stand for a month. The tube was then sealed off at C, C′, the alloy was melted and run into E, and the salts were mixed. No colour appeared, and after keeping three years still no change had taken place; the tube was then opened, when the red colour appeared. The contents of another tube, which had been kept the same time and had accidentally contained some mercury, turned black on exposure to the air. No doubt the mercuric chloride (before drying) had been converted into a mercurous salt. The colour was the same as obtained on adding excess of potassium iodide solution to a solution of a mercurous salt.

Speed of the Reaction.—It is seen from these experiments that the reaction between mercuric chloride and potassium iodide takes place at an enormously greater rate than that between lead chloride and potassium iodide in the same conditions. The cause of the difference is at first sight not clear. The possible factors which may influence the rate of the reaction are: (1) quantity of water present; (2) solubility; (3) volatility; (4) degree of ionisation when in solution. It is not necessary to consider the state of subdivision, as the salts were all prepared in the same way. Solubility appears to be an important factor, for, on referring to the list of salts at the beginning of this paper, it is seen that the least soluble salts show the least action. Mercuric chloride is roughly 10 times as soluble as lead chloride, but this would not account for the very great difference in the speed of the two reactions. The degree of ionisation of mercuric chloride in solution is extremely small, and this would have the opposite effect to that actually found. The volatility still remains to be considered; it is, undoubtedly, the determining factor, as shown by the following experiments:—In a wide tube constricted in the middle were placed, on one side some mercuric chloride, and on the other side potassium iodide. The tube was then sealed off and

watched from day to day. After the lapse of a month the margin of the potassium iodide was slightly coloured, and after three years the colour had travelled about 1 inch along the potassium iodide. The mercuric chloride remained free from colour. A similar experiment with lead chloride and potassium iodide showed no colour whatever. The difference was still more marked in another experiment in which the tubes were exhausted to 0·1 mm. The mercuric chloride coloured the potassium iodide *at once*, whilst after a year the lead chloride had had no effect.

Sodium Carbonate and Barium Sulphate.

In order to investigate the effect of a high temperature on reactions between solid salts, it was necessary to select those that were non-volatile. Sodium carbonate and barium sulphate were chosen ; they have the further advantage that the extent of the reaction may be measured by extracting the mixture with water and estimating the sodium carbonate volumetrically.

Preliminary experiments were made in order to discover if any reaction took place during the process of extraction, and it was found that, if carried out quickly, there was no appreciable change. The following numbers were obtained :—

Taken.		Treatment.	Found Na_2CO_3.
Na_2CO_3.	$BaSO_4$.		
gramme.	gramme.		gramme.
0·454	1	Shaken with water 10 mins.	0·454
0·454	1	Allowed to stand with water 24 hrs.	0·443

Effect of Heating.

Taken.		Heated.		Found Na_2CO_3.
Na_2CO_3.	$BaSO_4$.	Hrs.	Temp.	
gramme.	gramme.			gramme.
0·841	1·045	5	300°—400°	0·820
0·705	0·8035	35	,,	0·657

Although the temperature was considerably below the fusing point of either salt, a marked reaction was thus found to take place. The heating was effected in a crucible without any precautions as to drying.

A mixture was then made of equivalent quantities of sodium carbonate and

barium sulphate; it was ground lightly in a mortar for 10 minutes, and dried over sulphuric acid. It was placed in a glass bulb at the end of a long tube, and heated in the vapour of bromnaphthalene (about 280°). The following are the results:—

Heated.	Na_2CO_3 originally present.	Na_2CO_3 found.
hrs.	gramme.	gramme.
35	0·2137	0·2155
54	0·5800	0·5831

At this temperature there is no sign of any decomposition.

The temperature of boiling sulphur (444°) was next tried. A mixture was used of two molecules Na_2CO_3 to one molecule $BaSO_4$.

Heated.		Na_2CO_3.		
		Originally present.	Found.	Per cent. converted.
	hrs.	gramme.	gramme.	
Series I	20	0·5703	0·5355	6·10
	40	0·3671	0·3177	13·46
	65	0·4838	0·3971	17·92
Series II	10	1·0224	0·9264	9·58
	16	0·8738	0·8057	7·79
	20	0·8655	0·7813	9·73
	40	0·4993	0·4581	8·25
	65	0·4970	0·4581	7·83

In the second series the mixture was somewhat drier than in the first, and the reaction appears to have ceased after a short time. The results are not very concordant, probably owing to irregularity in the quantity of moisture present.

In another series, a mixture of sodium carbonate and barium sulphate in molecular proportions was used. The salts were heated and allowed to

Heated.		Na_2CO_3.	
		Percentage converted.	Percentage left (calculated on total weight of mixture).
	hrs.		
Series III	10	10·92	27·84
	30	10·19	28·07
	60	11·60	27·62

stand over sulphuric acid before mixing. The mixture was then put into bulb tubes previously dried by exhausting with a water air-pump and heating at the same time. The tubes were sealed and heated in sulphur vapour.

Next a mixture was made of sodium sulphate and barium carbonate in molecular proportions, and was heated in sulphur vapour in order to discover whether the composition would become finally the same as in the last experiment :—

Heated.	Percentage Na_2CO_3 formed (on total weight of mixture).
hrs.	
10	2·89
30	3·04
60	3·11

It would appear that the reaction in this direction is very much slower than in the other, and that equilibrium had not been reached; but it is impossible to say whether the two pairs of salts were in exactly the same condition with regard to moisture or not. Probably equilibrium had not been reached in either case.

Effect of Heat on a Mixture of Sodium Carbonate and Barium Sulphate in the Absence of Moisture.

The substances were placed separately in a glass tube, and dried by heating and exhausting with a mercury pump. The salts were then mixed and heated 14 hours in sulphur vapour. The result was, sodium carbonate taken 0·3071 gramme, found 0·3074 gramme. Thus no action takes place in the absence of moisture.

Effect of Shaking.—A mixture of 0·593 gramme sodium carbonate and 1·419 grammes barium sulphate was shaken in a closed flask for 10 hours continuously. It was then found that 0·584 gramme sodium carbonate remained.

Effect of Percussion.—About 2 grammes of a mixture of two molecules Na_2CO_3 to one molecule $BaSO_4$ was placed in a heavy steel mortar with a closely fitting plunger as pestle. The latter was then hammered vigorously for 30 minutes, receiving about 900 strokes in all. On extracting with water, it was found that 4·87 per cent. of the sodium carbonate had been converted into sulphate.

Effect of Pressure.—W. Spring* investigated reactions between sodium

* 'Bull. Soc. Chim.,' vol. 46, p. 166, and vol. 44, p. 299.

carbonate and barium sulphate, and between sodium sulphate and barium carbonate, under high pressures, and found that the extent of the reaction depended on the number of compressions and the time during which the mixture was left after compression.

These results were confirmed by the following experiments:—A mixture of two molecules Na_2CO_3 to one molecule $BaSO_4$ was subjected in the steel mortar to a pressure of 82 tons (equivalent to 104 tons per square inch). It was then found that 1 per cent. of the sodium carbonate had been converted into sulphate. It should be noted, however, that the mortar broke, so that the duration of the pressure was very short. In another experiment the pressure was 44·4 tons (56 tons per square inch, or about 8000 atmospheres), and its duration was 1 minute. The compressed mixture was then allowed to stand five weeks, when it was found that 4·02 per cent. of the carbonate had been converted. Spring found that, after the mixture had been subjected to a pressure of 6000 atmospheres, and then left a month, 3·84 per cent. barium sulphate had been converted into carbonate. It was found by Spring that mixtures of approximately the same composition were obtained, whether starting with barium sulphate and sodium carbonate or sodium sulphate and barium carbonate, thus showing that equilibrium had been attained. I have therefore confined myself to endeavouring to discover the effect of pressure on very thoroughly dried salts. The heavy mortar was first used. In order to dry the mixture, a hole was drilled sideways into the bottom of the mortar, and into this was cemented a tube containing phosphorus pentoxide. Molten wax was poured over the top of the plunger. However, the phosphorus pentoxide did not remain dry, and the result was that after the mixture had stood 23 days, and then been subjected to a pressure of 40 tons (equivalent to 51 tons per square inch, or 7600 atmospheres), 1·6 per cent. of the sodium carbonate had been converted into sulphate.

In the next experiment the plunger passed through a rubber cork which fitted into the mouth of the mortar, and air and moisture were pumped out through the side tube. The drying was not complete owing to a slight leak, and to the impossibility of shaking the powder. The result showed that 0·5 per cent. of the sodium carbonate had been converted into sulphate by a pressure of 40 tons.

Owing to the difficulty of drying the salts in the heavy mortar, a lighter one was made in which the salts could be hammered, the blow of a hammer being essentially the same as a high pressure exerted for a very short time.

Effect of Percussion on thoroughly dried Salts.—A steel mortar was

made of 1⅜-inch internal diameter, with a loosely-fitting piston, and the piston rod passed through a rubber cork fitting tightly into the mouth of the cylinder. Several grammes of the mixture were placed at the bottom of the cylinder, and were dried by gentle heating and shaking, and at the same time exhausting the cylinder with a Fleuss pump. The piston was then hammered vigorously for 30 minutes (about 900 strokes). On analysing the mixture it was found that only 0·1 per cent. of the sodium carbonate had reacted, an amount within the limits of experimental error. An exactly similar experiment was then made without specially drying the mixture; the salts had been dried over sulphuric acid, then mixed and kept in a well stoppered bottle. In this case 2·38 per cent. of sodium carbonate was converted into sulphate. The amount converted when the heavy mortar was used (*vide supra*) was 4·87 per cent. The areas of the pistons in the two cases were approximately as 1 : 2, *i.e.*, roughly the same as the extent of the reaction.

Influence of other Solvents.

Methyl Alcohol Vapour.—Lead chloride and potassium iodide were dried separately over phosphorus pentoxide, then mixed in a special apparatus and exposed to the action of methyl alcohol vapour, the liquid having been carefully dried by quicklime. The mixture acquired a strong yellow colour in about one hour.

Benzene Vapour.—When exposed to benzene vapour in a similar way, no change took place.

A similar experiment with mercuric chloride and potassium iodide gave a similar result, except that the mixture gradually turned black owing to the reducing action of the metallic sodium left in the tube to dry the benzene.

Chloroform Vapour.—Some lead chloride was placed at the closed end of a wide glass tube. Inside the tube two sealed thin-walled tubes were placed, one containing potassium iodide and the other pure chloroform, each previously dried by phosphorus pentoxide. The wide tube was then exhausted by the mercury pump and sealed off. On breaking the inner tubes, there was no apparent change of colour, either when the mixture was exposed to the action of the vapour or to that of the liquid. After standing a week a faint colour appeared. (Commercial phosphorus pentoxide was used in this experiment, so that the drying was not very perfect.)

Ammonia.—Some ammonia gas was dried over lime, and allowed to stand with phosphorus pentoxide (Kahlbaum's) in a glass bulb. The bulb was then sealed off and placed, together with a small bulb containing dry potassium iodide, in a wide tube containing lead chloride. The wide tube was then

heated, exhausted, and sealed off. On breaking the inner tubes, no change was observed, and after keeping for a year it was still unaltered.

With regard to the action of these solvents, methyl alcohol dissolves and ionises both salts, benzene and chloroform dissolve neither, whilst liquid ammonia dissolves and ionises potassium iodide, but forms an insoluble compound with lead chloride.*

Summary and Conclusion.

(1) Salts in the solid state usually undergo double decomposition when mixed (and not specially dried).

(2) Reaction between solid salts is accelerated by (1) heat, (2) pressure (including percussion), (3) shaking (no doubt by bringing fresh surfaces into contact).

(3) The solubility and volatility of the salts greatly influence the reaction-velocity.

(4) In the complete absence of water or other ionising solvent (*i.e.*, a solvent which becomes a conductor of electricity owing to the presence of the salt), *no reaction takes place.*

It would appear from these results that reaction between solid salts is of essentially the same nature as that between salts in solution. The quantity of water required to bring about a reaction is extremely minute, but its action is probably to ionise the salts. I would suggest that the water present forms a film on the surface of the salts, and that in this film minute quantities of the salts dissolve and there react. On this assumption, heat would accelerate reaction by increasing the solubility of the salts, and also by increasing their volatility if they had an appreciable vapour pressure. Pressure would in general bring more salt into solution, but would act chiefly by bringing the surfaces of the solids into close contact. Volatility would assist the reaction by carrying the particles of the volatile salt into contact with the surface of the other salt.

In the latter part of this work I have received most valuable assistance from Mr. J. H. Davies, B.Sc., to whom I here wish to express my indebtedness. I wish also to thank Professor A. C. Elliott for the use of the testing machine in the engineering department of this college.

* 'Amer. Chem. Journ.,' 1898, vol. 20, p. 820.

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Constants of Explosion of Cordite and of Modified Cordite.

By ROBERT ROBERTSON, M.A., D.Sc.

(Communicated by Col. Holden, R.A., F.R.S. Received January 10,—Read February 8, 1906.)

(Abstract.)

Objects of the Investigation.—These were to determine, under the conditions of pressure obtaining in a gun, the constants of explosion of cordite and of modified cordite, with special reference to the effects produced by the non-explosive ingredients, mineral jelly and acetone. The large increase in the percentage of guncotton which characterises modified cordite causes the retention of a greater quantity of volatile matter than was found in the older cordite; the nature of this volatile matter and its effects on the constants of explosion are examined.

Apparatus and Procedure.—The bomb, made to the design of Colonel Holden, F.R.S., at the Royal Gun Factory, had a chamber capacity of 128·32 c.c., was made of gun steel of about 3·3 cm. in thickness, and was fitted with arrangements for obturation and electrical insulation of the firing-pin and for drawing off the gases, which worked well in practice (diagram accompanies paper). The calorimeter and method of ascertaining the water equivalent of the apparatus are described (diagram), as are also the procedure when a shot is fired (diagram) and the means adopted for collecting and measuring the gases evolved (diagram).

Results. The results are embodied in a number of tables and include analyses of the explosive and of the volatile matter contained in it, the calories per gramme (water liquid and water gaseous), analyses of the gases evolved, the theoretical temperature of explosion (on the basis of the alteration of specific heat of the gases according to the data of Mallard and Le Chatelier), the theoretical pressure and the heat of formation of the explosives from the elements at constant pressure.

Calculations of the heat developed by the explosive are made from the heats of formation of the constituents of the explosive and products of its decomposition, and it is shown that the results so obtained are in good agreement with the actual calorimetric results. For the purpose of this calculation a special determination of the constants of Waltham Abbey guncotton was made.

Consequent on the change in composition from cordite to modified cordite,

the following are among the differences brought out, namely, a decrease in heat of 200 calories, and in temperature of explosion of 300° C.—facts which have a bearing on the decreased erosion found with the latter explosive—an increase in volume of gas and changes in the character of the gases.

The effect of the presence of mineral jelly in both natures of cordite is examined, as to the great diminution of heat, increase in volume of gases, etc., that result.

In a similar way the effect of the varying quantities of volatile matter found in modified cordite is investigated as to the constants of explosion. It is shown that in the modified cordite actually made the water in the volatile matter is practically constant, variations being due to acetone retained. Decrease in heat evolved, increase in gases and differences in composition of these gases due to the presence of acetone, are some of the results brought out in this part of the work.

Note is also made of the alterations in the constants of explosion due to increasing the density loading from 0·1 to 0·2.

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The Spontaneous Crystallisation of Binary Mixtures. — Experiments on Salol and Betol.

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In a previous paper by the present authors, it was shown that, for the aqueous solutions of certain salts, a definite curve may be traced which gives the temperature of spontaneous crystallisation for a supersaturated solution of any given strength. "Spontaneous crystallisation" is to be understood to signify that, at and below these temperatures, crystallisation may be started by purely mechanical means. This curve, to which they have given the name of "supersolubility curve" (SH or sH of fig. 1), is, for the salts examined by them, nearly parallel to the solubility curve (ME or mE of fig. 1), and generally separated from it by an interval of about 10°. To use Ostwald's phraseology, it indicates, on the temperature-concentration diagram, the boundary between the area representing the "metastable" condition, in which crystallisation can only take place in contact with a solid crystal, and the area representing the "labile" condition, in which crystallisation may take place spontaneously.

Previous investigators have usually endeavoured to trace the process of

crystallisation in alloys, fusion mixtures, and solutions, by determining the constitution of the solid which separates. We have endeavoured rather to determine the changing constitution of the liquid, making use of the refractive index for this purpose. The curve was traced, not only by means of the refractive index, which attains a maximum value at the temperature of spontaneous crystallisation, but also by the development of a dense cloud of crystals, which makes its appearance at the same temperature when the solution is stirred. This we term a " labile " shower, in order to distinguish it from the much thinner "metastable" showers, which may occur before
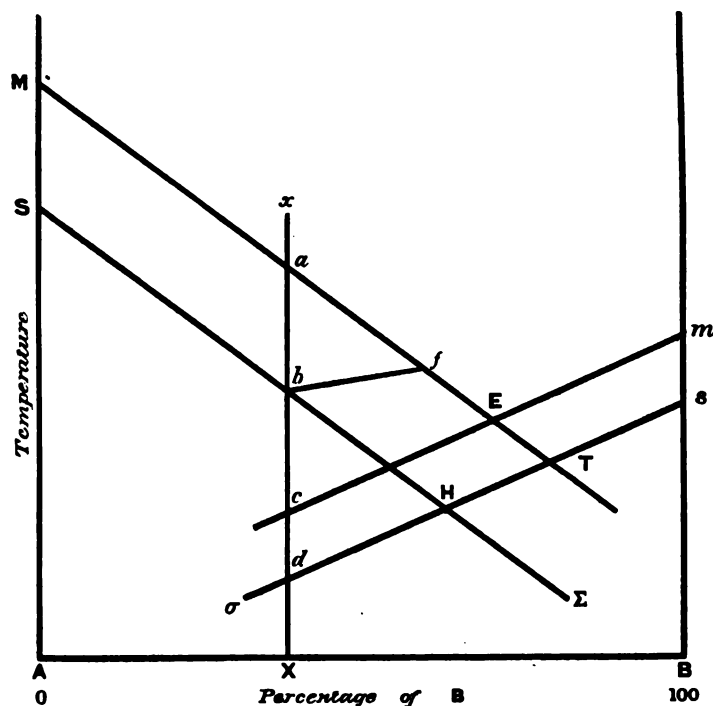
Fig. 1.

this temperature is reached. Solutions enclosed in sealed tubes, so as to be preserved from chance inoculation by dust of the crystalline solid, cannot be made to crystallise by shaking at any temperature higher than that given by the supersolubility curve.

Subsequent experiments (not yet published) have traced similar super-solubility curves for mixtures of aqueous solutions of such substances as sodium nitrate and lead nitrate.

In none of these experiments was it possible to carry the observations down to the temperature at which the other component, water, begins

to separate in the solid form. We have, however, endeavoured to determine the temperature of spontaneous crystallisation for pure supercooled water,[*] and have shown reason to believe that it is not far from that of the maximum index.

. The present investigation was undertaken with the object of tracing the supersolubility curves for mixtures of two substances, in which the freezing-point curves of the two components can be determined down to the eutectic temperature and below it. If such curves can be traced, it may be predicted that the conditions of crystallisation will be indicated by the accompanying diagram, in which M and m are the melting points of the components A and B respectively, E is their eutectic point, and ME, mE are their solubility curves. S and s are the solidifying points, or the temperatures at which A and B freeze spontaneously; and SH, sH are the supersolubility curves meeting in what we call the "hypertectic point" H. The changes in a cooling liquid initially of composition x containing excess of A, and protected from inoculation by A, will in general be represented by a movement of the figurative point, which denotes the temperature and constitution of the liquid, along the line XabfE, the first crystals making their appearance at b. But the diagram shows that the liquid, if sufficiently rapidly supercooled, may exhibit no less than four freezing points, a, b, c, d, of which c represents the separation of the constituent B if the solid phase B be present, and d its spontaneous separation; and none of these coincides with the eutectic temperature.

Multiple freezing points are not unusual in alloys. In his paper on "Surfusion in Metals and Alloys,"[†] Roberts-Austen remarks that some alloys seem to have three freezing points, but concludes that one of these coincides with the eutectic temperature.

In most experiments upon alloys and other mixtures, it has been usual to prevent any appreciable supersaturation by inoculating the liquid and by keeping it agitated; or, when experiments have been made with supercooled liquids, they have generally been cooled far below the supersolubility curves in order to determine the rate of growth at lower temperatures.

The substances chosen for our experiments were salol, the phenyl salicylate, which melts at $42\frac{1}{2}°$, and betol, the β-naphthol salicylate, which melts at about 92°.

* 'Chemical News,' 1906, vol. 94, p. 89.
† 'Roy. Soc. Proc.,' 1898, vol. 63, p. 452.

I. The Crystalline Form of Salol and Betol.

The form of salol obtained from solution in alcohol has been determined · by Wyrouboff* and Milch† as orthorhombic; the crystals occur in plates of rhombic outline, tabular owing to the predominance of {010}, having their edges bevelled by {111} and {212}. The angle of the rhomb is 71° 30'; the double refraction is very strong; a positive bisectrix is perpendicular to (010); the plane of the optic axes (which are inclined at a wide angle) contains the axes b and c, and is therefore parallel to the shorter diagonal of the rhombic plate.

Examined under the microscope, a drop of solution of salol in ether readily yields rhombic plates possessing these characters.

Tammann‡ mentions three different modifications of salol (I, II, and III), melting respectively at 42°, 38°·8, and 28°·5. I is the commercial salol, II he describes as forming between 0° and 37°, and III at −20°. In the course of these experiments, we have not observed more than one modification, namely, that whose melting point was found to be 42°·5, which is described in this paper on p. 333. Salol II has not been observed, and the temperature has not been sufficiently low to produce the Salol III mentioned by Tammann.

The form of betol has not hitherto been determined. We find that, from solution in ether, it readily crystallises in plates, belonging to the monoclinic system, which are parallelograms having a plane angle of 84°. These plates are due to the predominance of {010}, and have their edges bevelled by {110} and {011}. The double refraction is very strong; a positive bisectrix is perpendicular to (010); and the plane of the optic axes (which are inclined to one another at a wide angle) makes an angle of 17° with the edge [010 : 011]. Some crystals also show faces of {012}.

The measured angles are—

$$010 : 110 = 75° \ 28'$$
$$010 : 011 = 55° \ 11\tfrac{1}{2}'$$
$$100 : 011 = 84° \ 38'$$

from which—

$$a : b : c = 0\cdot26094 : 1 : 0\cdot69980$$
$$\beta = 83° \ 27\tfrac{1}{2}'$$

The obtuse bisectrix makes an angle of 11° with the normal to (100), and of 72\tfrac{1}{2}° with the normal to (001).

In the following experiments upon the crystallisation of salol and betol

* 'Bull. Soc. Min.,' 1889, vol. 12, p. 443.

† 'Liebig's Ann.,' 1893, vol. 273, p. 82.

‡ 'Zeit. Phys. Chem.,' 1899, vol. 29, p. 71.

from the molten substances, and from their mixtures, salol always crystallised in the open trough in white discs or aggregates of discs, often forming spherical groups or large circular plates. Drops of the various liquids were also examined under the microscope, during crystallisation, when the individual crystals of salol presented the appearance sometimes of rounded or perfectly circular discs, sometimes of rhombic plates. These always showed a positive bisectrix perpendicular to the plane of the plate; and there is no reason to doubt that the discs are of the same material as the plates, which they resemble also in refraction and birefringence. The rhombic plates only appeared in mixtures not far removed from the eutectic in composition. In all other drops, salol crystallised in rounded discs. Pure salol, when rapidly supercooled to about 6°, yielded large rhombic plates having the form and optical properties described above. There is, therefore, no evidence that in our experiments salol crystallises in more than one modification.

Betol always crystallised in the open trough in the form of fine fibres, or in spherical tufts of fibres radiating from a centre. When a drop of a mixture containing excess of salol was allowed to crystallise under the microscope, it was possible to distinguish the betol from the salol, not only by the contrast between fibres and discs, but also by the fact that salol crystals, having nearly the same refractive index as the liquid, are nearly invisible when viewed by ordinary light, whereas the betol fibres are easily seen. The question now arises whether these fibres are identical with the crystals obtained from solution in ether; Tammann mentions four varieties of betol, I, II, III, and IV, two melting at 95°, the others at 93° and 91° respectively.

In the course of these experiments, we have observed three modifications of betol: (A) The monoclinic plates described above, derived from solution in ether, which appear to melt at about 92°; (B) tufts which melt at about 90°; (C) plates of rhombic outline having a plane angle of 71°, which extinguish at an angle inclined at about 3° to the longer diagonal of the rhomb, and are positively birefringent. The plates (C) showed an optic axis on the edge of the field and an acute (?) bisectrix not perpendicular to the plates. They appeared to melt at about the same temperature as the monoclinic plates (A) described above. These plates (C) only appeared as extremely small rhombs, with the obtuse angle truncated, in a mass of betol which had been allowed to crystallise very slowly between 80° and 90°, and since all the experiments on spontaneous crystallisation mentioned in this paper take place at temperatures lower than 80°, it is not probable that these rhombs crystallised in any of the mixtures examined.

The tufts (B) usually appeared spontaneously when a drop of betol was supercooled to the temperature of the room, whereas the plates (A) appeared at a higher temperature and scarcely grew at all in a cold drop. Occasionally needle-shaped crystals appeared in the betol drops, and also thinner plates which formed in a ring round the plates (A), and extinguished uniformly with them between crossed nicols. These polarised in bright colours, but did not show any regular form. When heated, however, the whole mass liquefied at precisely the same temperature; the needles and thin plates are, therefore, probably the same as the plates (A) mentioned above.

We have made several microscopic experiments with betol. If the fibres (B) be introduced into a drop of liquid betol at about 15°, they continue to grow as fibres. If, on the other hand, a plate of betol (A) (obtained from solution in ether) be introduced, its growth is scarcely perceptible, neither does it appear to be dissolved. The same is true of liquid mixtures containing both salol and betol. This suggests that throughout these experiments the betol (B) which crystallises from fused substance, or from its mixtures with salol, is not identical with the crystals (A) obtained from solution in ether, and it is certainly not identical with the crystals (C) which form above 80°. It is probably the modification IV which Tammann describes as melting at 91°.

II. The Temperature of Spontaneous Crystallisation of Salol.

(a) *Experiments with Sealed Tubes.*

Salol was enclosed in sealed glass tubes which were heated until the substance had completely melted. Some of the tubes contained fragments of glass together with the salol, and others contained salol alone. These tubes were shaken continually in a cooling water bath, but absolutely failed to recrystallise, though the temperature of the bath was lowered to 12°, and the salol became very viscous. Some of the tubes were kept for nine months and still remained uncrystallised. (One of the tubes was broken open at the top after three weeks and kept in the court of the University Museum in air presumably free from salol germs. The salol in it crystallised after three days and nights. It is possible, however, that the crystallisation really began at the top of the tube at the time when it was broken open.) When a sealed tube containing salol was heated in such a way as to melt all the substance, with the exception of a few very small crystals at the top of the tube, the salol recrystallised, when shaken, in a dense shower at approximately 30°, and soon became solid. The density of the shower indicated that this may be about the temperature of spontaneous crystallisation.

(b) *Stirring in an Open Vessel.*

Experiments were next made on the refractive index, in order to determine whether this exhibits a maximum value at the temperature of spontaneous crystallisation, as appears to be possibly the case with water.

In these experiments, the inverted goniometer described in ' Phil Trans.,' 1903, vol. 202, p. 464, was used. The trough was filled with liquid salol at about 50°, and a glass prism was immersed in it. The index of the salol as it cooled was determined from time to time by the method of total internal reflection within the prism.

The first experiment was carried out in a room in which salol had never been previously used, so that the air was presumably free from salol germs. The liquid was stirred rapidly in the trough as it cooled by means of a small platinum stirrer driven by a water motor.

The refractive index rose steadily from 1·580563 at 38°·5 to 1·589681 at 20°·5. No well-marked break occurred at any point of the index-temperature curve, and no crystals made their appearance. If the liquid has really passed through the temperature of spontaneous crystallisation, there is no clear evidence of a sudden change in the index at this point. The salol was quite clear and liquid at 20°·5; it then very suddenly became solid with a considerable rise of temperature. Although this experiment was repeated several times, the salol never again reached nearly so low a temperature as 20°·5 without solidifying. The reason may possibly be that the air was subsequently impregnated with salol germs which start crystallisation in the liquid at, or somewhat below, the melting-point temperature.

In a second experiment the salol, after being fused and heated to 90°, was placed in the goniometer trough at 60°, and was kept stirred. The index rose from 1·575916 at 50° to 1·584131 at 33°. At 55° one small crystal appeared in the trough, at 40° crystals were growing rapidly along the bottom edge of the trough, and at 34° the salol was growing round the prism. At 33° a thick shower of crystals suddenly appeared and the stirring was stopped. This shower caused the temperature to rise, and the index to fall in value till it reached 1·582096 at 38°. The density of the shower in the trough rendered further readings for the index impossible, and at 40° the salol was almost solid.

In a third similar experiment the index rose from 1·572970 at 56° to 1·584184 at 33°. Crystals first appeared at 41° along the bottom edge of the trough and grew rapidly. At 33° a dense shower of crystals occurred. The temperature rose and the index fell till it reached 1·580831 at 40°. Two other experiments gave similar results. In each experiment, the index

rose till the temperature reached 33°, when a dense cloud of crystals occurred, causing a rise in temperature and a fall in index. Crystals first appeared in the trough at 43° and 40° respectively, round the prism or at the bottom of the trough.

From these experiments we conclude that the temperature of spontaneous crystallisation for salol is 33°, since at this temperature a dense shower occurs, and the index attains a maximum value. The fall in index observed in these experiments at 33° is probably solely due to the rise of temperature consequent on the spontaneous development of the shower of crystals. This is indicated by fig. 2, in which the downward branch of the index-
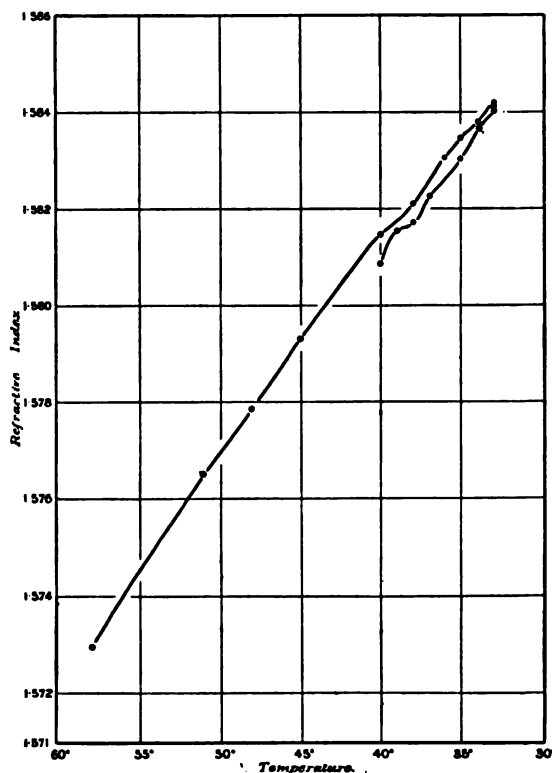
FIG. 2.

temperature curve, showing the behaviour of the salol after the maximum index has been reached and the shower of crystals has fallen, coincides very nearly with the upward branch of the curve which shows the behaviour of the salol before the shower took place. The slight difference of a degree between the two branches of the curve may be due simply to the fact that on one branch the temperatures are read in a cooling liquid and on the other

in a liquid of which the temperature is rising. In the first experiment quoted above, it is probable that the substance passed far into the labile state without crystallising, like the salol in sealed tubes.

(c) *Crystallisation by Means of Friction in a Closed Tube.*

If 33°· is the temperature of spontaneous crystallisation, it ought to be possible to make salol solidify in a closed tube at this temperature by mechanical means. With this viscous liquid, shaking with fragments of glass is not sufficient, and more violent friction seems to be necessary. By the following contrivance we were enabled to preserve the salol from the possibility of inoculation from the air, and yet to apply actual scratching to the sides of the tube in which it was contained.

Salol was introduced into a U-tube, closed at one end. A long brass wire, with a piece of platinum wire attached to its further end, was passed into the U-tube so that the salol at the closed end could be scratched by moving the wire to and fro from outside. The U-tube was inverted and completely immersed in a water bath and kept for some time at about 80°. It is certain, therefore, that there is no solid salol within the tube. The water bath and the immersed tube were then allowed to cool gradually, and the part containing the liquid salol was continually scratched. The salol remained quite clear and liquid till the temperature reached 33°, when it suddenly crystallised along the lines of scratch.

This experiment was repeated several times with the same result, the salol always crystallising at 33°.

This result is in complete accordance with the evidence derived from the sudden appearance of the labile cloud at 33°, when the liquid was stirred in an open trough: and we are, therefore, justified in regarding 33° as the temperature of spontaneous crystallisation of salol, thus fixing one point upon the supersolubility curve.

Tammann has traced the variation of the velocity of crystallisation with temperature for salol between the temperatures 20°·6 and 37°·8. He found the velocity of crystallisation to increase as the temperature fell. On plotting his results as a curve, with velocity of crystallisation as ordinates and temperature as abscissæ, it will be seen that at 31°·4 there is a distinct break in the continuity of the curve. This break probably corresponds to the temperature of spontaneous crystallisation. The break in the velocity-of-crystallisation-temperature curve is at a temperature slightly below 33°, but it is probable that in measuring the rate of crystallisation of liquid salol along a tube, the latent heat raised the temperature slightly, in spite of the precautions taken to keep the temperature constant, and that the break in

this curve at 31°·4 really coincides with the spontaneous crystallisation at 33°.

III. THE TEMPERATURE OF SPONTANEOUS CRYSTALLISATION OF BETOL.

(a) *Experiments with Sealed Tubes.*

In order to determine the temperature of spontaneous crystallisation, betol was first enclosed in sealed glass tubes. As in the experiments with salol, some of the tubes contained angular fragments of glass together with the betol, and some contained betol alone. The tubes were heated for some time in boiling water to melt all the betol, and were then shaken by hand in a hot water bath, which was allowed to cool slowly.

The betol in the tubes, without the glass fragments, failed to crystallise, although shaken in the water bath till the temperature reached 15°. The betol became more and more viscous as the cooling proceeded, and at 15° appeared to be a jelly.

An hour later it started crystallising slowly, the crystals beginning at the edges of the tube, and gradually spreading until the whole was solid.

The tubes containing fragments of glass with the betol crystallised in a dense labile shower at about 75°. These experiments were repeated with a larger water bath, so that the tubes could be shaken more violently.

The betol was then always found to crystallise at 79°. The tubes without the angular glass fragments enclosed in them failed, as before, to crystallise till the temperature was far lower; 79°, therefore, appears to be the temperature of spontaneous crystallisation for betol; it will be found that this conclusion is supported by the subsequent experiments.

The liquid betol is sufficiently viscous to require the friction of the glass within the tube, as well as mere shaking, to start crystallisation when it becomes labile. Friction within the sealed tube was also found necessary in some aqueous solutions, for example, sodium chlorate.[*] The refractive index of liquid betol has not at present been determined, owing to the comparatively high temperature at which it melts.

(b) *Stirring in an Open Vessel.*

The betol was heated in a small beaker to 140° to melt it completely. A thermometer was immersed in the beaker, the liquid was stirred by a platinum vane driven by an electric motor, and the temperature was allowed to fall gradually. The experiment was repeated eight times, with the following results:—

[*] 'Journ. Chem. Soc.,' vol. 89, 1906, p. 441.

1. The betol crystallised between 90° and 92° in two of the experiments, *i.e.*, at approximately the melting point.

2. The betol crystallised in a dense labile shower at 79° in three experiments.

3. The betol crystallised at temperatures below 79° three times, namely, at 74°, 63°, and 52°. In the experiments where betol crystallised at the melting point, it was noticed that a little had solidified round the upper edges of the beaker above the liquid before the stirring began.

This probably inoculated the liquid, which then began to crystallise at the melting point in the metastable condition. In three experiments, the betol crystallised spontaneously at 79°, the temperature at which it crystallises in a sealed tube.

In the three remaining experiments, the substance crystallised spontaneously at various temperatures below 79°. Now the viscosity of betol renders it very liable to supercooling, as has been shown in the sealed tube experiments without glass fragments, when it was cooled to the temperature of the room, and remained for some hours without crystallising.

From all the experiments, then, it results that 79° is the highest temperature at which betol can be made to crystallise by mechanical means, and this is, therefore, to be regarded as the temperature of spontaneous crystallisation, fixing one point upon the supersolubility curve.

Tammann has also measured the velocity of crystallisation of betol at different temperatures. Most of his experiments are made below 70°, but, for his betol I, the velocity of crystallisation is given for temperatures between 80°·5 and 65°·2. On plotting his results as a curve, with velocity of crystallisation as ordinates, and temperature as abscissæ, it is seen that the velocity of crystallisation reaches a distinct maximum at 78°. This probably corresponds to the temperature of spontaneous crystallisation for betol, which has been shown above to occur at 79°. The maximum velocity of crystallisation appears to be reached at a slightly lower temperature than the spontaneous crystallisation, but, as has been mentioned in the case of salol, the latent heat must raise the temperature of the betol slightly, as it grows in the tube, and the two temperatures are probably really identical.

IV. The Solubility or Freezing-point Curve for Salol and Betol in each other.

The next experiments were designed to determine the solubility curve for betol and salol in each other, in other words, the freezing-point curve of their mixtures, which defines the limit between the metastable and unsaturated regions.

(a) *The Melting Point of Salol.*

The melting point of salol was determined as the temperature of approximate equilibrium between the liquid and the solid substance by the following method.

A few grammes of salol were placed at the bottom of a small open test-tube, the tube was corked and placed in boiling water for several minutes till the salol had completely melted. The tube was then allowed to cool slowly in a large glass beaker filled with hot water, and from time to time the liquid was inoculated with a minute crystal of salol. After the crystal had been introduced, the tube was shaken continually by hand, and the salol crystal was watched with a lens, being illuminated by an electric lamp placed immediately behind the beaker. The liquid was first inoculated at 50°, when the small salol crystal was seen to dissolve immediately. The liquid was again inoculated at 48°·5, 47°, 46°, and 45°, and each time the crystal dissolved immediately. On inoculating at 44° and 43°, the crystal dissolved more slowly, but again disappeared completely on shaking. On inoculating at 42°·5, however, the small salol crystal, on shaking, formed a slight " metastable " shower in its neighbourhood, the shower increasing in density as the salol cooled.

This experiment was repeated several times, and the salol crystal was always seen to form the same shower directly the temperature reached 42°·5. At any temperature slightly higher than 42°·5, the introduced crystal dissolved completely. From these experiments the melting point of salol was taken to be 42°·5. Previous determinations by a different method by Ostwald[*] gave the melting point as 39°·5. Tammann[†] gives, as stated above, 42°, 38°·8, and 28°·5 for three modifications of the substance; and it was determined by Seifert[‡] as 42° to 42½°.

(b) *The Melting Point of Betol.*

Precisely the same method was employed to find the melting point of betol, using both the monoclinic plates obtained from solution, and also the tufts obtained from fusion.

(1) *Inoculation with Betol Plates.*—When the liquid betol was inoculated at 95°, the crystal immediately dissolved. Betol crystals also dissolved in the liquid at 94°, 93°, and 92°·5. When the liquid was inoculated at 92°, the crystal appeared neither to grow nor to dissolve, and at 91°·5 it formed a slight metastable shower when shaken in the tube. A distinct shower also

[*] 'Zeits. Phys. Chem.,' 1897, vol. 22, p. 290.

[†] 'Zeits. Phys. Chem.,' 1899, vol. 29, p. 71.

[‡] 'Journ. Prakt. Chem.,' 1885, vol. 31, p. 473.

formed if the betol was inoculated at 91° or 90°. The same experiment was repeated several times, and the result was always the same. The betol crystal dissolved in the liquid at 92°·5, neither grew nor dissolved at 92°, and formed a slight metastable shower around itself at 91°·5. The melting point of betol plates was, therefore, taken to be 92°.

(2) *Inoculation with Tufts of Betol obtained from Fusion.*—When liquid betol was inoculated at 95°, 94°, 93°, 92°, and 91°, the small betol tufts dissolved. At 90° the betol formed a slight metastable shower, which became denser at 89°. The same result was obtained on repeating the experiment.

The melting point of the betol tufts was therefore taken to be 90°. Previous determinations by Tammann gave the melting point as 93° and 91°, these temperatures relating, perhaps, to the above two modifications of betol. When heated on a microscope slide, the tufts were found to melt at a slightly lower temperature than the plates.

(c) *Solubility of Salol in Betol.*

Mixtures containing weighed quantities of salol and betol were placed in open test-tubes. The tubes were corked and heated in boiling water till the mixtures had completely melted. They were then allowed to cool slowly in a large glass beaker of hot water and, as they cooled, the liquid mixtures were inoculated from time to time with a minute crystal of salol. The behaviour of this crystal was watched with a lens in precisely the same way as in the experiments on the melting points described above. The tubes were continually shaken by hand in the water bath as the mixtures cooled. In general, for each mixture the crystal of salol at first dissolved when the liquid in the test-tube was inoculated with it, and this continued until a certain definite temperature was reached.

The introduced salol crystal then no longer dissolved, but formed a slight metastable shower in its neighbourhood when the tube was shaken, as was very clearly seen with a lens. The temperature at which this slight shower first occurred in each mixture when inoculated with salol was taken to be the temperature of saturation with regard to salol.

The following are the results of the experiments on the solubility of salol in betol :—

Each experiment was repeated several times. The numbers corresponding to the experiments are given in fig. 3.

Experiment 1. $\left\{\begin{array}{l}\text{Salol} = 90 \text{ per cent.}\\ \text{Betol} = 10 \text{ per cent.}\end{array}\right\}$. The mixture inoculated with

salol at 42°·5, 42°, 40°, and 39° dissolved the crystal at once. Inoculated at 38° yielded a slight metastable shower on shaking. The mixture is, therefore, saturated with respect to salol at 38°.

Experiment 2. $\left\{\begin{array}{l}\text{Salol} = 78 \text{ per cent.} \\ \text{Betol} = 22 \text{ per cent.}\end{array}\right\}$. Inoculated at 38°, 36°, 35°, 34°, and 33°, dissolved the crystal. Inoculated at 32°·5 yielded a slight metastable shower. The mixture is, therefore, saturated with respect to salol at 32°·5.

Experiment 3. $\left\{\begin{array}{l}\text{Salol} = 74 \text{ per cent.} \\ \text{Betol} = 26 \text{ per cent.}\end{array}\right\}$. Inoculated at 40°, 39°, 37°, 35°, 33°, and 32°, dissolved the crystal. Inoculated at 31° yielded a metastable shower. The mixture is, therefore, saturated with respect to salol at 31°. ‑

Experiment 4. $\left\{\begin{array}{l}\text{Salol} = 70 \text{ per cent.} \\ \text{Betol} = 30 \text{ per cent.}\end{array}\right\}$. Inoculated at 37°, 35°, 34°, 33°, 32°, 31°, and 30°, dissolved the crystal. Inoculated at 29° yielded a slight metastable shower. The mixture is, therefore, saturated with respect to salol at 29°.

Experiment 5. $\left\{\begin{array}{l}\text{Salol} = 52\cdot035 \text{ per cent.} \\ \text{Betol} = 47\cdot965 \text{ per cent.}\end{array}\right\}$. Inoculated with salol at 30°, this mixture immediately yielded a thick labile shower of betol (?) This shower differs completely in appearance from the slight metastable shower obtained by inoculating the mixtures at the temperature of saturation, the whole mixture becoming quite opaque suddenly, and soon solidifying; 30° is, therefore, probably below the temperature of spontaneous crystallisation of betol in this mixture. In order to maintain the mixture in liquid form below this temperature, it was heated again to about 70°, and then cooled suddenly to 25° without solidifying. It was inoculated with a salol crystal at 25°. The crystal dissolved, but, shortly after, a shower of betol occurred throughout the tube. The same thing happened when the mixture was cooled suddenly to 24°, 23°, or 22°. The introduced salol crystal dissolved, and then a betol shower occurred. When cooled suddenly to 21°·5, and inoculated with salol, it yielded a slight metastable shower of salol (?). The same effect was produced when the mixture was cooled to 21°, 20°, or 19°, and inoculated with salol. This experiment was repeated several times, and 21°·5 was the highest temperature at which the slight metastable shower occurred when the liquid was inoculated with a salol crystal. This mixture was, therefore, only just saturated with respect to salol at 21°·5, although supersaturated with respect to betol. The point given by this mixture lies on the freezing-point curve for salol in betol as determined by the four preceding experiments, but it must lie considerably below the supersolubility curve for betol in salol. These results, together with the melting point

for salol ascertained above, determine the freezing-point curve of salol in betol.

(d) *Solubility of Betol in Salol.*

Precisely the same method was employed to determine the solubility of betol in salol. The liquid mixtures were inoculated from time to time with a betol crystal until the crystal, as it dissolved, began to yield a fine dusty metastable shower of betol needles. Each experiment was repeated several times. The following descriptions relate to inoculation with a monoclinic plate of betol. A number of the experiments were repeated with tufts of betol obtained from fusion. The temperatures determined with these are so nearly the same as the temperatures determined with the plates that they are not shown upon the diagram. The difference never exceeded half a degree and the temperatures were sometimes above and sometimes below those determined by the plates.

Experiment 6. $\left\{ \begin{matrix} \text{Salol} = 10\cdot01 \text{ per cent.} \\ \text{Betol} = 89\cdot99 \text{ per cent.} \end{matrix} \right\}$. Inoculated with a crystal of betol at 90°, 88°, and 87°, dissolved the crystal. Inoculated at 86° yielded a slight metastable shower in the neighbourhood of the crystal. The mixture is, therefore, saturated with respect to betol at 86°.

Experiment 7. $\left\{ \begin{matrix} \text{Salol} = 20\cdot11 \text{ per cent.} \\ \text{Betol} = 79\cdot89 \text{ per cent.} \end{matrix} \right\}$. Inoculated at 85°, 84°, 83°, 82°·5, and 82°, dissolved the crystal. Inoculated at 81° yielded a slight metastable shower. The mixture is, therefore, saturated with respect to betol at 81°.

Experiment 8. $\left\{ \begin{matrix} \text{Salol} = 30\cdot34 \text{ per cent.} \\ \text{Betol} = 69\cdot66 \text{ per cent.} \end{matrix} \right\}$. Inoculated at 85°, 82°, 80°, 78°, 77°, and 76°, dissolved the crystal. Inoculated at 75° yielded a slight metastable shower. The mixture is, therefore, saturated with respect to betol at 75°.

Experiment 9. $\left\{ \begin{matrix} \text{Salol} = 41\cdot54 \text{ per cent.} \\ \text{Betol} = 58\cdot46 \text{ per cent.} \end{matrix} \right\}$. Inoculated at 75°, 72·5°, 71°, 69°, and 68°, dissolved the crystal. Inoculated at 67° yielded a slight metastable shower. The mixture is, therefore, saturated with respect to betol at 67°.

Experiment 10. $\left\{ \begin{matrix} \text{Salol} = 50\cdot43 \text{ per cent.} \\ \text{Betol} = 49\cdot57 \text{ per cent.} \end{matrix} \right\}$. Inoculated at 67°, 65°, 63°, 62°, 61°, and 60°, dissolved the crystal. Inoculated at 59° yielded a slight metastable shower. The mixture is, therefore, saturated with respect to betol at 59°.

Experiment 11. $\left\{\begin{array}{l}\text{Salol} = 52\cdot035 \text{ per cent.} \\ \text{Betol} = 47\cdot965 \text{ per cent.}\end{array}\right\}$. Inoculated at 62°, 60°, 59°, and 58°, dissolved the crystal. Inoculated at 57°·5 yielded a slight metastable shower. This mixture is, therefore, saturated with respect to betol at 57°·5.

Experiment 12. $\left\{\begin{array}{l}\text{Salol} = 59\cdot98 \text{ per cent.} \\ \text{Betol} = 40\cdot02 \text{ per cent.}\end{array}\right\}$. Inoculated at 57°, 55°, 53°, 52°, and 51°, dissolved the crystal. Inoculated at 50° yielded a slight metastable shower. This mixture is, therefore, saturated with respect to betol at 50°.

Experiment 13. $\left\{\begin{array}{l}\text{Salol} = 70 \text{ per cent.} \\ \text{Betol} = 30 \text{ per cent.}\end{array}\right\}$. Inoculated at 48°, 47°, 46°, 45°, 44°, 43°, and 42°, dissolved the crystal. Inoculated at 41° yielded a very slight metastable shower. This mixture is, therefore, saturated with respect to betol at 41°.

Experiment 14. $\left\{\begin{array}{l}\text{Salol} = 74 \text{ per cent.} \\ \text{Betol} = 26 \text{ per cent.}\end{array}\right\}$. Inoculated at 41°, 40°, 39°, and 38°, dissolved the crystal. At 37°·5 yielded a slight metastable shower. This mixture is, therefore, saturated with respect to betol at 37°·5. This is the mixture that gives the hypertectic point on the supersolubility curve (p. 338). It has already been shown to be saturated with respect to salol at 31° (p. 335).

Experiment 15. $\left\{\begin{array}{l}\text{Salol} = 78 \text{ per cent.} \\ \text{Betol} = 22 \text{ per cent.}\end{array}\right\}$. Inoculated with betol at 37°, 36°, 35°, 34°, and 33°, dissolved the crystal. Inoculated at 32°·5 yielded a slight metastable shower. This mixture is, therefore, saturated with respect to betol at 32°·5. It has already been shown to be saturated with respect to salol at the same temperature (p. 335). This mixture is, therefore, the eutectic.

Experiment 16. $\left\{\begin{array}{l}\text{Salol} = 80\cdot2 \text{ per cent.} \\ \text{Betol} = 19\cdot8 \text{ per cent.}\end{array}\right\}$. Inoculated at 37°, 36°, 34°, 32°, and 31°, dissolved the crystal. Inoculated at 30° yielded a slight metastable shower. This mixture is, therefore, saturated with respect to betol at 30°.

Experiment 17. $\left\{\begin{array}{l}\text{Salol} = 90 \text{ per cent.} \\ \text{Betol} = 10 \text{ per cent.}\end{array}\right\}$. Inoculated with betol at 32°, 30°, and 29°, dissolved the crystal. Inoculated at 28°, the whole mixture suddenly crystallised, on slightly shaking, in a dense labile shower of salol (?). Therefore, the temperature of spontaneous crystallisation of salol in this mixture appears to be 28°. In order to cool the mixture below this temperature of spontaneous crystallisation, without the labile shower taking

place, it was heated to 70°, and suddenly cooled to 18°·5 by immersion in a cold water bath. When introduced at this temperature the betol dissolved, as also when introduced into the mixture at 18°. At 17°·5 the introduced betol crystal formed a slight metastable shower, and a few minutes later the whole mixture solidified suddenly in a labile shower. During this experiment the mixture was kept for an hour and a-half at 18° without beginning to solidify. This experiment was repeated several times;
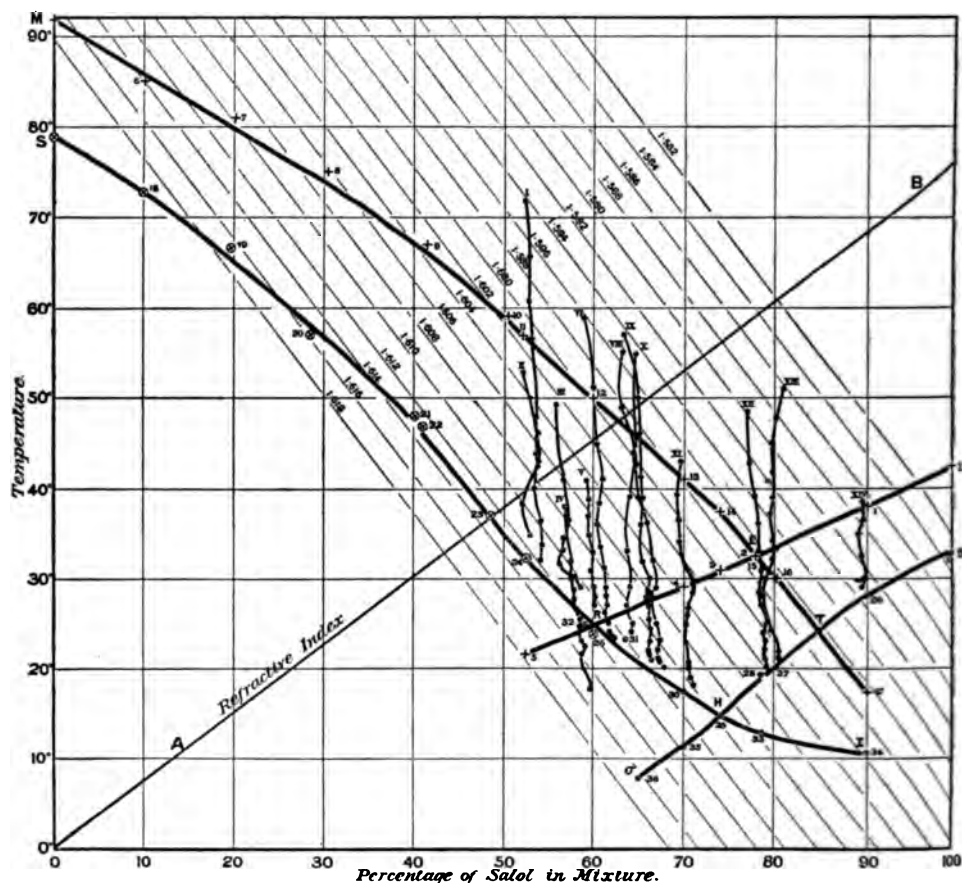
Fɪɢ 3.

generally, the inoculation with betol at temperatures varying from 22° to 17° brought down immediately a labile shower of salol quite unlike the slight metastable shower produced by inoculating the mixtures at the temperature of saturation. Once or twice, however, on inoculating this mixture with betol at 19° and 18°, the crystal dissolved, and on inoculating again at 17°·5 the betol at first formed a slight metastable shower. This slight shower invariably brought down the labile shower almost immediately

afterwards; $17°·5$, being the highest temperature at which the metastable shower appears, is, therefore, the temperature of saturation of this mixture with respect to betol. It is to be noted that the experiment always failed if the mixture was allowed to cool gradually, as the labile shower then invariably came down at $28°$.

To these results must be added the experiment which determines the melting point of betol, namely, $90°$ for the tufts (B) or $92°$ for the plates (A). The 13 experiments taken together give the freezing-point curve of betol in salol. In fig. 3 the curve is drawn to the melting point of betol (A); it would really accord better with the observations if drawn to the melting point of (B).

This series of experiments, together with the series giving the freezing-point curve of salol in betol, determine the complete solubility curve for all mixtures of salol and betol.

This curve, MEm on fig. 3, consists of two branches crossing at the eutectic point E where the composition is salol $= 78$ per cent., betol $= 22$ per cent. at $32°·5$, the branches then continuing down uniformly even below the supersolubility curve SHs.

Inoculation experiments are indicated by a cross.

Sealed tube experiments „ „ cross in circle.

Stirring experiments „ „ dot in circle.

Refractive index observations are indicated by a thick dot.

V. The Supersolubility Curves for Mixtures of Salol and Betol

Experiments upon the temperature of spontaneous crystallisation of mixtures of salol and betol were next undertaken, in order to determine for these mixtures the supersolubility curve.

The experiments were conducted in two ways:—

1. By noting the temperature of spontaneous crystallisation of mixtures in sealed tubes when cooled and shaken in a water bath.

2. By observing the temperature at which the dense shower of crystals ("labile shower") occurs in a mixture which is being rapidly stirred. These experiments were made in the goniometer trough, and were used also for the determination of the refractive index.

By these experiments the temperature of spontaneous crystallisation has been ascertained for a large series of mixtures, and the supersolubility curve has been completely determined.

(a) *Experiments with Sealed Tubes.*

Weighed quantities of betol and salol were enclosed in sealed glass tubes, together with angular fragments of glass. They were heated in boiling water until the mixture was completely liquid, and then shaken as they cooled in a hot water bath. When the temperature of the bath had fallen to a certain point, a thick shower of small crystals suddenly appeared in the tube, after which the whole mixture soon became solid. This temperature is, therefore, taken to be the temperature of spontaneous crystallisation of the mixture under examination.

Each such mixture gives a point on the supersolubility curve.

The following are the results obtained, each experiment being repeated several times:—

Experiment.	Constitution of liquid.	Temperature of spontaneous crystallisation.
	Per cent.	°
18	{ Salol = 10 ·035 { Betol = 89 ·965	73 ·0
19	{ Salol = 19 ·754 { Betol = 80 ·246	66 ·5
20	{ Salol = 28 ·443 { Betol = 71 ·557	57 ·0
21	{ Salol = 40 ·0 { Betol = 60 ·0	48 ·0
22	{ Salol = 40 ·8 { Betol = 59 ·2	47 ·0
23	{ Salol = 48 ·17 { Betol = 51 ·83	37 ·0
24	{ Salol = 52 ·6 { Betol = 47 ·4	32 ·0
25	{ Salol = 60 ·1 { Betol = 39 ·9	24 ·0

To these results must be added the experiment with pure betol, which has been shown above to crystallise spontaneously in a glass tube at 79°. The nine results, when plotted on a concentration-temperature diagram, are seen to lie very approximately on a continuous curve, which forms part of one branch of the supersolubility curve (fig. 3). It was not possible to plot the entire supersolubility curve by the method of sealed tubes, for this method failed when the mixture contained a larger proportion of salol than about 60 per cent. Some mixtures, which were very rich in salol, behaved like pure salol, and did not crystallise at all, and in others, containing from 65 to 75 per cent. salol, the betol crystallised out after the lapse of a few days in round globules, leaving the salol still liquid.

Some other method, therefore, had to be adopted in order to plot the

remainder of the supersolubility curve for mixtures containing more than 60 per cent. of salol.

(b) *Stirring in an Open Vessel.*

With aqueous solutions of salts, it has been shown that·when such a solution is stirred as it cools, the refractive index rises to a maximum value and then falls again. At the maximum point a dense shower of crystals generally forms throughout the whole mass of the solution. This "labile" shower is quite different from the thin "metastable" shower of isolated crystals, which may have been formed earlier. The temperatures corresponding to the maximum index and the labile shower determine the supersolubility curve.

An attempt was therefore made to investigate, in the same way, mixtures of salol and betol containing more·than 60 per cent. salol, by observing whether the mixtures (1) possess a maximum refractive index, (2) exhibit the dense shower of crystals on reaching this maximum.

Various mixtures were made up and their refractive indices determined in the trough of the inverted goniometer by means of an immersed glass prism, as described on p. 328. The mixtures were placed in the trough at about 60°, and were stirred vigorously with the platinum stirrer. In all these experiments it was found that the refractive index rose very rapidly as the mixture cooled till the temperature reached a certain point, when a dense shower of very small crystals occurred throughout the liquid. The mixture then rapidly became opaque and soon solidified completely. The shower of crystals was always extremely dense and remained suspended in the viscous liquid instead of falling to the bottom of the trough, so that determinations of the refractive index became almost impossible after this point. The shadow denoting total reflection became gradually fainter and less well defined till it disappeared completely.

The density of the cloud rendered it impossible to ascertain for certain whether the refractive index really attains a maximum value at this temperature. The occurrence of the shower was, therefore, the only available indication of the temperature of spontaneous crystallisation; and the refractive indices of the various mixtures are of no service in the determination of the supersolubility curve. They will, however, be considered in a later paragraph, together with the results of further experiments on the refractive indices of mixtures of salol and betol.

The following results, obtained from stirring the mixtures in the goniometer trough, give the temperatures at which the shower occurs in the various mixtures, and determine the form of the supersolubility curve. In every experiment the liquid was thoroughly stirred while cooling :—

Experiment.	Constitution of mixture.	Temperature of spontaneous crystallisation.
	Per cent.	°
26	{ Salol = 89·99 Betol = 10·01 }	28·0
27	{ Salol = 80·19 Betol = 19·81 }	20·1
28	{ Salol = 78·43 Betol = 21·57 }	19·3
29	{ Salol = 73·997 Betol = 26·003 }	15·0
30	{ Salol = 69·968 Betol = 30·032 }	17·5
31	{ Salol = 63·27 Betol = 36·73 }	23·5
32	{ Salol = 58·9 Betol = 41·1 }	25·0

To these must be added the experiment with pure salol which solidified in the trough in a shower at 33°. Experiments 29 to 32 yield a continuation of the curve already obtained by another method in Experiments 18 to 25, and if the whole series 18 to 32 be plotted on a concentration-temperature diagram, they will determine the complete supersolubility curve for the whole series of possible mixtures of salol and betol. This curve is seen to consist of two branches, meeting at 15° in the hypertectic point, where the constitution is 74 per cent. salol, 26 per cent. betol, and the temperature is the highest at which both salol and betol can crystallise spontaneously together.

(c) *Spontaneous Crystallisation below the Hypertectic Temperature.*

Not only has it proved possible to trace the two branches of the solubility curve ME*m* below their intersection at the eutectic point E, but also the branches of the supersolubility curve SH*s* below their intersection at the hypertectic point H. It will be seen from the diagram that any mixture which gives a point on a branch of the supersolubility curve for one component below the hypertectic temperature must, as it cooled, have already passed through a point on the other branch of the supersolubility curve for the other component at a temperature above the hypertectic. In order, therefore, to obtain a point on the supersolubility curve below the hypertectic, it is necessary to chill the mixture suddenly below the temperature at which the labile shower corresponding to the higher branch of the curve should make its appearance.

The method of suddenly cooling a mixture has already been used in determining the branches of the solubility curve at points below the supersolubility curve.

In the following experiments the cooling mixtures were stirred in an open vessel, and the temperature at which a dense labile shower occurred was noted :—

Experiment 33. The mixture $\left\{\begin{array}{l}\text{salol} = 78\cdot5 \text{ per cent.}\\ \text{betol} = 21\cdot5 \text{ per cent.}\end{array}\right\}$, which becomes labile with respect to salol at 19°, was chilled suddenly from a high temperature to 18°, and then allowed to cool gradually. A dense labile shower of betol occurred at 13°, 13°, 12°·5, 12°·5, in four different experiments. If, therefore, the labile shower of salol be prevented at 19°, betol will begin to crystallise spontaneously at 13°.

Experiment 34. Mixture $\left\{\begin{array}{l}\text{salol} = 90 \text{ per cent.}\\ \text{betol} = 10 \text{ per cent.}\end{array}\right\}$, which becomes labile with respect to salol at 28°, was chilled suddenly from a high temperature to 18°, and then allowed to cool gradually. A dense labile shower of betol occurred at 10°, 10°·5, 10°·5, 10°·5 in four experiments. If, therefore, the labile shower of salol at 28° be prevented, betol will begin to crystallise spontaneously at 10°·5. The temperature of this mixture rose to 24° on solidifying.

Experiment 35. Mixture $\left\{\begin{array}{l}\text{salol} = 70 \text{ per cent.}\\ \text{betol} = 30 \text{ per cent.}\end{array}\right\}$, which becomes labile with respect to betol at 17°·5, was chilled suddenly from a high temperature to 15°, and then allowed to cool gradually. A dense labile shower of salol occurred at 11°·5 in three experiments. If, therefore, the labile shower of betol at 17°·5 be prevented, salol will begin to crystallise spontaneously at 11°·5.

Experiment 36. Mixture $\left\{\begin{array}{l}\text{salol} = 64\cdot99 \text{ per cent.}\\ \text{betol} = 35\cdot01 \text{ per cent.}\end{array}\right\}$, which becomes labile with respect to betol at 21°·5, was chilled suddenly from a high temperature to 15°, and then allowed to cool gradually. A dense labile shower of salol occurred at 8° in three experiments. If, therefore, the labile shower of betol be prevented at 21°·5, salol will begin to crystallise spontaneously at 8°.

In Experiments 35 and 36 the shower appears at first to be composed of fairly large, clear crystals of salol. Betol, however, comes down also in characteristic tufts as soon as the shower has started. In the Experiments 33 and 34 the shower that first occurs has the appearance of betol.

It will be seen that the four points determined by Experiments 33 to 36 lie on the prolongation of the supersolubility curves determined by the previous experiments.

The whole of the concentration-temperature diagram is now divided up into several different areas :—

1. In the region above the curve MEm all the mixtures are unsaturated.

2. In the region below the curve SHs all the mixtures are so highly supersaturated with respect to betol or to salol, or to both, that they are labile, and can be made to crystallise by appropriate mechanical means.

Of this labile region, the portion within the curve SHσ is labile with respect to betol, but not with respect to salol; the portion within the curve sHΣ is labile with respect to salol, but not with respect to betol; whilst the portion below the curve σHΣ is labile with respect to both salol and betol, being below both branches of the supersolubility curve.

3. Between the two regions (1) and (2) in the space MSHsmEM, all the mixtures are metastable, and if the appropriate crystal be introduced it will continue to grow in the mixture.

Of this metastable region, the portion MSRE is supersaturated with respect to betol, but not with respect to salol; the portion mETs is supersaturated with respect to salol, but not with respect to betol; whilst the portion RETH is supersaturated with respect to both salol and betol.

VI. The Refractive Indices of Mixtures of Salol and Betol.

In the course of the experiments described above, the refractive indices of the mixtures were determined as they cooled by means of total reflection within a dense glass prism immersed in the liquid mixture, from the time when the mixture was first placed in the trough until the occurrence of the dense shower at the temperature of spontaneous crystallisation. Beyond this point the determination of the refractive index was generally impossible owing to the dense labile shower.

In general, for mixtures containing from 60 to 100 per cent. of salol, the index rises regularly as the temperature falls from about 50° or 60° to the temperature of spontaneous crystallisation, and there is no break in the continuity of the index-temperature curve denoting any physical change taking place in the liquid.

Mixtures containing from 50 to 60 per cent. of salol occasionally exhibit slight irregularities in their index-temperature curves as they cool, probably because they are somewhat more viscous owing to the amount of betol they contain ; and this may give rise to more intense concentration streams. The streams can be clearly seen rising round the immersed prism in mixtures containing a large proportion of betol, even while the liquid is being stirred. In a few of the mixtures containing from 50 to 60 per cent. of salol the index appears to reach a maximum, and then to begin to fall ; but the labile shower always occurs at this point and renders the determination difficult. Some of the mixtures do not exhibit an actual maximum, but the index-temperature

curve shows a slight change in direction near the temperature of spontaneous crystallisation. The refractive indices of mixtures containing more than 50 per cent. betol have not yet been investigated, owing to the difficulties introduced by concentration streams and the high temperatures of spontaneous crystallisation.

The occurrence of the thick labile shower is not always accompanied by an appreciable rise in temperature. The following are the only cases in which a marked rise of temperature was observed :—

1. Pure salol, which crystallises spontaneously at 33°, rose to 40° during solidification in the trough.

2. The mixture 89·99 per cent. salol, 10·01 per cent. betol, which crystallises spontaneously at 28°, rose to 33° during the occurrence of the labile shower.

3. The mixture 80·19 per cent. salol, 19·81 per cent. betol, which crystallises spontaneously at 20°, was observed to rise to 21° during the labile shower.

Mixtures containing more than this percentage of betol showed no appreciable rise of temperature during solidification.

4. When a liquid crystallised on a portion of the supersolubility curve below the hypertectic point, there was a considerable rise of temperature on solidification.

The following are the results of the experiments on the refractive indices of mixtures of salol and betol. All the mixtures were stirred unless otherwise stated.

We only give here the general results of the experiments; the actual observations are shown by the thick dots on the Curves I to XIV in fig. 3, which correspond to the following descriptions. No. VII is omitted on the diagram in order to avoid confusion with V and VI :—

Experiment I. $\left\{ \begin{array}{l} \text{Salol} = 52\text{·}024 \text{ per cent.} \\ \text{Betol} = 47\text{·}976 \text{ per cent.} \end{array} \right\}$. The index rose from 1·594172 at 72° to 1·611860 at 32°. The mixture was unstirred; betol first appeared at 40°. At 32° the growth of betol became very rapid and spread throughout the mixture.

Experiment II. $\left\{ \begin{array}{l} \text{Salol} = 52\text{·}04 \text{ per cent.} \\ \text{Betol} = 47\text{·}96 \text{ per cent.} \end{array} \right\}$. The index rose from 1·603139 at 53° to 1·610987 at 35°; betol first appeared at 38°·5 and in a thick shower at 34°.

Experiment III. $\left\{ \begin{array}{l} \text{Salol} = 56 \text{ per cent.} \\ \text{Betol} = 44 \text{ per cent.} \end{array} \right\}$. The index rose from 1·602733 at 49°·5 to 1·610570 at 31°·5. The index then remained nearly constant till the temperature fell to 29°. A thick shower appeared at 30°.

Experiment IV. $\begin{Bmatrix} \text{Salol} = 56\cdot51 \text{ per cent.} \\ \text{Betol} = 43\cdot49 \text{ per cent.} \end{Bmatrix}$. This mixture was examined in an ordinary hollow prism and was not stirred. It becomes labile at 28°, but in this case it was possible to trace the change in index far into the labile region. The index rose from 1·607443 at 38° to 1·615239 at 17°·5. Crystals first appeared at 28° (exactly on the supersolubility curve) and grew very fast in straight lines down the corners and faces of the prism. The main part of the mixture, however, was still liquid at 17°·5.

Experiment V. $\begin{Bmatrix} \text{Salol} = 58\cdot9 \text{ per cent.} \\ \text{Betol} = 41\cdot1 \text{ per cent.} \end{Bmatrix}$. The index rose from 1·604440 at 41° to 1·610358 at 27°. A very slight shower occurred at 33° and a thick labile shower at 25°.

Experiment VI. $\begin{Bmatrix} \text{Salol} = 59\cdot986 \text{ per cent.} \\ \text{Betol} = 40\cdot014 \text{ per cent.} \end{Bmatrix}$. The index rose from 1·596093 at 59° to 1·610940 at 23°. The mixture became slightly dusty at 26°, and a shower took place at 25°. The stirring was then stopped, but the measurements were continued.

Experiment VII. $\begin{Bmatrix} \text{Salol} = 60 \text{ per cent.} \\ \text{Betol} = 40 \text{ per cent.} \end{Bmatrix}$. The index rose from 1·598022 at 54° to 1·610476 at 27°, then fell slightly, reaching 1·680216 at 25°; but the mixture became dusty at 28°, and the readings were difficult. The dense labile cloud occurred at 25°.

This same mixture, examined at rest, gave values somewhat lower than the above, showing a slight fall in index at 25°, followed by a rise up to 21°. Betol grew rapidly at the bottom of the trough at 25° and at lower temperatures. The prism was immersed in the upper part of the liquid.

Experiment VIII. $\begin{Bmatrix} \text{Salol} = 63\cdot27 \text{ per cent.} \\ \text{Betol} = 36\cdot73 \text{ per cent.} \end{Bmatrix}$. The index rose from 1·595523 at 55° to 1·609248 at 24°. The mixture became slightly dusty at 24°, and a thick shower fell at 23°. This experiment was repeated with the same mixture unstirred, when values were obtained for the indices differing slightly from those previously obtained, being generally less by about 5 in the fourth place of decimals.

The same mixture was also examined in a hollow prism, when the values obtained agreed more closely with those of the stirred mixture. Crystals first appeared at 23°·5 and grew rapidly; the index at 23° being 1·609354. The index continued to rise as the temperature fell, till it reached 1·611131 at 18°·4, the mixture being now far in the labile region.

Experiment IX. $\begin{Bmatrix} \text{Salol} = 65\cdot033 \text{ per cent.} \\ \text{Betol} = 34\cdot967 \text{ per cent.} \end{Bmatrix}$. The index rose from

1·594301 at 57° to 1·609538 at 20°·7. The mixture became very dusty at 22°; the stirring was then stopped, but the measurements were continued.

Experiment X. $\left\{\begin{array}{l}\text{Salol} = 65·38 \text{ per cent.}\\\text{Betol} = 34·62 \text{ per cent.}\end{array}\right\}$. The index rose from 1·594494 at 55° to 1·608946 at 20°. The mixture became a little dusty at 21°, and a dense labile shower occurred at 20° after stirring for 10 minutes at this temperature.

Experiment XI. $\left\{\begin{array}{l}\text{Salol} = 69·968 \text{ per cent.}\\\text{Betol} = 30·032 \text{ per cent.}\end{array}\right\}$. The index rose from 1·597173 at 43° to 1·607967 at 18°·2. At 18°·2 the mixture became slightly dusty, and at 17°·5 a dense labile shower occurred.

Experiment XII. $\left\{\begin{array}{l}\text{Salol} = 78·43 \text{ per cent.}\\\text{Betol} = 21·57 \text{ per cent.}\end{array}\right\}$. The index rose from 1·589902 at 48°·5 to 1·602199 at 19°·3. The mixture became slightly dusty at 20°, and a thick labile shower occurred at 19°·3.

The same mixture was examined in the trough unstirred, and the values agreed very closely with those previously obtained. The observations were carried on till the index reached 1·603283 at 17°. The mixture was then in the labile state, but no crystals were visible.

Experiment XIII. $\left\{\begin{array}{l}\text{Salol} = 80·19 \text{ per cent.}\\\text{Betol} = 19·81 \text{ per cent.}\end{array}\right\}$. The index rose from 1·586235 at 51° to 1·601143 at 20°. A slight dusty shower appeared at 20°·1 and a dense labile shower at 20°. The temperature then rose from 20° to 21°.

Experiment XIV. $\left\{\begin{array}{l}\text{Salol} = 89·99 \text{ per cent.}\\\text{Betol} = 10·01 \text{ per cent.}\end{array}\right\}$. The index rose from 1·586847 at 38°·5 to 1·591357 at 29°. At 28° a dense labile shower occurred and the temperature rose 5°.

From these experiments it will be seen that—

1. Mixtures containing a large percentage of betol have a higher index than those containing less betol at the same temperature.

2. Mixtures, when stirred, give a thick labile shower at temperatures which, as shown by the sealed tube experiments on mixtures containing excess of betol, correspond to the supersolubility curve SH*s* of the diagram.

Unstirred solutions do not usually yield profuse crystallisation until they have entered far into the labile state. An example is No. IV on fig. 3.

3. Mixtures containing from 100 per cent. to 60 per cent. of salol exhibit no indication of a maximum refractive index at the temperature of spontaneous crystallisation. Mixtures containing less than 60 per cent. of

salol do yield indications of a maximum index, at the temperature of spontaneous crystallisation, but the evidence is not conclusive.

If the changes in refractive index for each mixture after crystals have begun to appear be left out of account, the above experiments will enable us to ascertain the refractive index of any given mixture at any desired temperature.

The results may be expressed by curves drawn with concentrations as abscissæ, and temperatures as ordinates, the refractive index being constant for each curve. Such curves were drawn for the following values of refractive index: 1·590, 1·592, 1·594, 1·596, 1·598, 1·600, 1·602, 1·604, 1·606, and 1·608.

The concentration-temperature curves for the different values of the index were found to be very approximately straight lines parallel to each other and inclined to the concentration-axis at an angle 52° 30', the scale being such that a length representing 10 per cent. on the concentration axis represents 10° on the temperature axis.

The perpendicular distance between any two of these curves was found to be proportional to the difference in the corresponding refractive indices. Hence if a line AB be drawn on the concentration-temperature diagram (fig. 3) inclined at an angle 37° 30' to the concentration axis, the refractive index of any mixture as it cools may be measured along this line in the same way as the temperature is measured along the vertical axis. Any point on the diagram will therefore give the concentration and temperature of a mixture by its co-ordinates measured along the vertical and horizontal axes, and its refractive index measured along the line AB.

The whole series of observations in the above experiments on the refractive indices of the mixtures may now be plotted on the diagram. It must be remembered that in all these experiments in the open trough the liquid was liable to inoculation from the air of the laboratory, so that crystals always made their appearance in the metastable state; but it will be seen from the curves, which are numbered I to XIV in fig. 3, that the separation of crystals, before the labile shower appears, affects the concentration but little.

Some of the curves exhibit slight irregularities on crossing the solubility curves of betol and salol, they then continue straight down the diagram till they reach the supersolubility curve SH s, where the labile shower, in general, takes place. Those curves representing the behaviour of mixtures containing from 50 to 70 per cent. of salol appear to bend slightly to the right on reaching the supersolubility curve.

VII. CONCLUSION.

The experiments described in this paper indicate that for a knowledge of what actually occurs during the crystallisation of a binary mixture, a consideration of the supersolubility curve is equally necessary with that of the freezing-point curve: unless supersaturation be prevented by mechanical agitation and by inoculation with both constituents. And even then, unless the cooling be very slow, a sudden access of one constituent will occur when its supersolubility curve is reached.

In most experiments upon alloys and other mixtures, agitation and inoculation have hitherto been employed. But in the actual solidification of such mixtures and of natural rocks the conditions cannot in general be favourable for solidification as a eutectic. In rocks, the absence of the eutectic structure has often been commented upon.

It will be observed that the liquid which, under normal conditions, may really be expected to yield the eutectic structure is that of which the composition corresponds to the hypertectic point H (figs. 1 and 3). The eutectic liquid E will, in general, as it cools, reach one branch of the supersolubility curve before it reaches the other, and the corresponding constituent will crystallise first.

If a mixture of salol and betol, having the eutectic composition, be allowed to crystallise on a microscope slide, it will solidify mainly in large plates of salol, overgrown and partly penetrated by fibres of betol of later growth. But if the hypertectic mixture be allowed to crystallise under the same conditions, it will solidify as an intimate mixture of the two substances.

We have also prepared microscopic sections of various mixtures after they have completely solidified in test-tubes, with the following results:—

(1) *Eutectic Mixture, stirred while solidifying at a Temperature below that at which it becomes Labile* (about 15° C.).—This yielded a mass consisting of an intimate mixture of salol and betol.

(2) *Hypertectic Mixture, stirred while solidifying at a Temperature at which it is Labile* (about 15° C.).—This yielded a still more intimate fine-grained mixture of salol and betol than was obtained from the eutectic.

(3) *Eutectic crystallised at Rest while Labile.*—The section was an intimate mixture, but not so fine grained as No. 1.

(4) *Hypertectic crystallised at Rest while Labile.*—The section was an intimate mixture, but not so fine grained as No. 2.

(5) *Eutectic crystallised at Rest while Metastable* (25° C. to 30° C.).—The mixture was inoculated with both salol and betol, and occupied five days in crystallising.

The section showed well-defined and isolated groups of both salol and of betol, in the form of tufts or radiating discs.

(6) *Mixture containing* 65 *per cent. Salol and* 35 *per cent. Betol, stirred and allowed to crystallise in the Labile Condition* (15°).—The section was an intimate mixture, scarcely distinguishable from (1) and (2).

(7) *Mixture containing* 90 *per cent. Salol and* 10 *per cent. Betol, stirred and allowed to crystallise in the Labile Condition* (15° C.).—The section consisted mainly of small crystals of salol, and showed very little betol.

No. 5 shows clearly that the eutectic mixture does not yield the eutectic structure except in the labile condition.

It will further be noticed that the four possible freezing points which ought to be exhibited in general by a cooling binary mixture are abundantly illustrated by the foregoing experiments. In one case they have been ascertained experimentally for one and the same mixture, namely, that having the composition 90 per cent. salol, 10 per cent. betol.

This mixture yielded crystals of salol by inoculation at 38° (p. 335), a labile shower of salol at 28° (p. 337), crystals of betol by inoculation when supercooled to 17°·5 (p. 338), and a labile shower of betol when supercooled to $10\frac{1}{2}$° (p. 343).

Finally, we may mention various anomalies in the work of previous observers, which may perhaps be explained by the results of our own experiments.

(1) Heycock and Neville, in their paper on "Complete Freezing-point Curves of Binary Alloys,"[*] mention two sorts of precipitates encountered when the copper-tin alloys were being stirred; one, the soft precipitate forming at the freezing point on the upper branch of their curve, and the other the abundant finely-gritty precipitate forming at the lower freezing points.

These probably correspond to our metastable and labile showers.

(2) Roberts-Austen[†] mentions the multiple freezing points of lead-tin alloys.

These probably correspond to points on our supersolubility curves.

(3) The sudden change in the velocity of crystallisation of salol and betol determined by Tammann occurs almost exactly at our temperatures of spontaneous crystallisation.

(4) A eutectic structure is not generally produced at the temperature of the eutectic point unless the mixture be inoculated and stirred.

This is what would be expected from our diagram.

* 'Phil. Trans.,' A, vol. 189, 1897, p. 50.

† 'Roy. Soc. Proc.,' 1898, vol. 63, p. 452.

It may be suggested that each branch of our supersolubility curve is merely the solubility curve of an unstable modification which appears as soon as the liquid is supersaturated with regard to it, and then at once becomes converted into the ordinary stable modification ; if this were so, the curves ought to meet the vertical lines corresponding to pure salol and pure betol at points giving the melting temperatures of these unstable modifications. The temperatures so determined are not actually the melting temperatures of any known modification of salol or betol, although several modifications have been recorded.

The Relation of Thallium to the Alkali Metals: a Study of Thallium Sulphate and Selenate.

By A. E. H. TUTTON, M.A., D.Sc., F.R.S.

In this communication are given the results of a crystallographical investigation of the normal sulphate Tl_2SO_4 and selenate Tl_2SeO_4 of thallium, similar to the author's previous researches on the normal sulphates and selenates of the alkali metals, potassium, rubidium, and cæsium, and of ammonium.[*] It thus completes the work commenced in the year 1893 on the series of normal sulphates and selenates $R_2{{S}\atop{Se}}O_4$.

Crystals of thallium sulphate, prepared by Lamy, were investigated in 1863 by von Lang,[†] who found them to be orthorhombic and isomorphous with those of potassium sulphate. The selenate does not appear to have been previously investigated, except that it was considered by Kuhlmann,[‡] and from preliminary observations of Des Cloiseaux and v. Lang, to be also isomorphous with potassium selenate, and that the molecular volume was determined by Petterssen.

The investigation of these two salts, especially as regards the optical part, has been a difficult matter, on account of the very small size of the crystals, due to their slight solubility, which is only four and two parts respectively in 100 parts of water at the ordinary temperature. Both salts

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[*] 'Journ. Chem. Soc.,' 1894, vol. 65, p. 628 ; 1897, vol. 71, p. 846 ; 1903, vol. 83, p. 1049 ; 1906, vol. 89, p. 1059.

[†] 'Phil. Mag.' (4), vol. 25, p. 248.

[‡] 'Bull. Soc. Chim.,' 1864 (1), p. 330.

crystallise from a hot aqueous solution in snow-white apparently opaque needles, useless for goniometrical purposes, which may be half an inch or more long in the case of the sulphate, but which are very small, even minute, in the case of the selenate. From solutions only slightly supersaturated small elongated plates separate, which are more suitable for goniometrical measurement. They are orthorhombic prisms, very thin perpendicular to the brachypinakoid, which thus vastly predominates. They are extremely highly reflective, affording quite unusually brilliant images of the signal slit of the goniometer, rendering them much more suitable for measurement than their unpromising appearance would lead one to suppose, and their adamantine lustre and translucency is, doubtless, also connected with this exceptional power of reflecting light.

The prism faces are often much striated, but an adequate number of crystals have eventually been obtained from a few crops out of the very many which have been prepared, which were quite free from striation or distortion of any kind, and which were also of adequate thickness to afford excellent reflections from most of the other faces as well as from those of the brachypinakoid.

The optical investigation, however, has met with grave obstacles, and it is only after very numerous failures that at length the necessary transparent section plates and prisms have been prepared, and the optical constants successfully determined. Moreover, the refractive indices of the two salts are so high, very nearly two, as to be higher than those of the immersion liquids, methylene iodide and mono-bromnaphthalene, usually employed in determinations of optic axial angles. Further, the specific gravity of both salts is twice as great as that of methylene iodide, so that the immersion method of Retgers cannot be employed for its determination. How all these exceptional difficulties have been overcome will be briefly explained under each particular heading.

Thallium Sulphate, Tl₂SO₄.

Preparation and Analysis.—The material started with consisted of specially purified thallium sulphate, supplied by Merck, which was several times recrystallised before use. A determination of the content of thallium in one of the crops employed in the investigation was made, by dissolving 0·9964 gramme in an adequate quantity of distilled water to ensure complete solution, converting it into thallium iodide TlI by addition of excess of potassium iodide solution, boiling to effect perfect decomposition, filtering off the yellow insoluble (in cold water) thallium iodide when quite cold on to a weighed filter paper, washing, drying at 100°, and weighing.

The weight of TlI thus obtained was 1·3130, which corresponds to 81·24 per cent. of thallium in the crystals of thallium sulphate. The calculated percentage is 80·96.

Solubility in Water.—Two determinations were made for the ordinary and boiling temperatures. The results showed that:—

100 grammes of water at 6°·5 dissolve 3·36 grammes of thallium sulphate.

100 „ „ 100° „ 19·14 „ „ „

These numbers are in substantial agreement with those of Lamy, which are 4·74 for 15° and 18°·5 for 100°.

Goniometry.

Crystal System.—Orthorhombic, holohedral class.

Habit.—Tabular parallel to $b = \{010\}$, and thin prismatic to acicular parallel to the axis a.

Ratio of Axes.—$a:b:c = 0·5555:1:0·7328$. Von Lang found $0·5539:1:0·7319$.

Forms observed.—$b = \{010\}$, $c = \{001\}$, $p = \{110\}$, $p' = \{130\}$, $q = \{011\}$, $q' = \{021\}$, $q''' = \{012\}$, $o = \{111\}$, $o' = \{112\}$.

The spherical projection common to the whole series of alkali sulphates and selenates, to ammonium sulphate, and to thallium sulphate and selenate, is given in fig. 1, and a typical crystal of thallium sulphate, as obtained
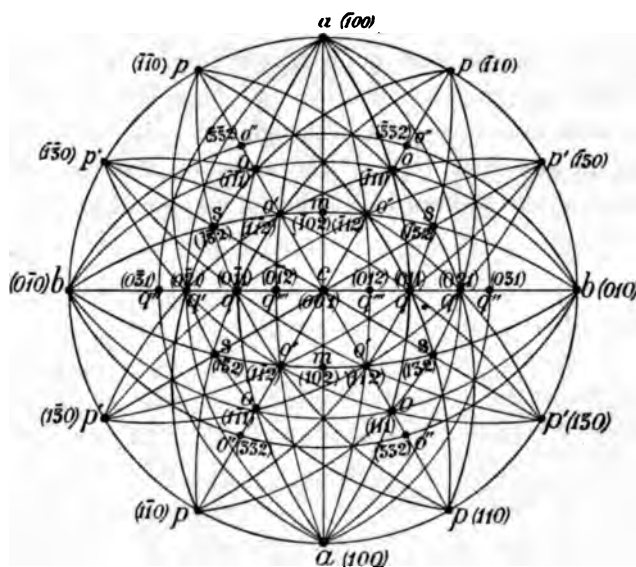
Fig. 1.

by crystallisation from only slightly supersaturated solutions, is shown in fig. 2.
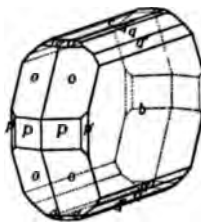
Fig. 2.

Crystal Angles.—The results of the measurements obtained with a dozen of the most perfect crystals, selected from four of the most satisfactory crops, are given in the accompanying table, together with the calculated values and the angular values found by von Lang.

The best developed form is invariably the brachypinakoid $b = \{010\}$, the prisms being usually relatively long thin plates parallel to and formed by the faces of this form, the length being parallel to the axis a. The reflections from these broad b-faces were generally excellent, as were also those from the narrower faces of the basal pinakoid $c = \{001\}$, the latter, indeed, being almost always perfect, affording absolutely single and very brilliant images of the signal slit. The faces of the intermediate primary brachy-prism $q = \{011\}$ in this elongated zone also yielded very good reflections, and to a somewhat less extent so also did those of the brachy-prism $q' = \{021\}$. The form $q''' = \{012\}$ was observed on four of the crystals measured, and the images were quite trustworthy. The primary pyramid $o = \{111\}$ is always the predominating end form, and the images yielded by its faces were also very good, although not quite so brilliant as those of the forms in the zone $[bqc]$. The faces of the secondary pyramid $o' = \{112\}$ were twice observed, and, although very small, yielded trustworthy reflections.

Morphological Angles of Thallium Sulphate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of von Lang.
ap = (100) (110)........	—	° ′ — ° ′	° ′	29 3	′	° ′
pp = (110) (1Ī0)........	2	57 57—58 8	58 3	58 6	3	
pp′ = (110) (130)........	—	—	—	29 59	—	
ap′ = (100) (130)........	—	—	—	59 2	—	
p′b = (130) (010)........	3	30 58—30 59	30 59	30 58	1	
pb = (110) (010)........	7	60 52—61 3	60 56	60 57	1	61 1
cq‴ = (001) (012)........	5	19 57—20 14	20 7	20 7	0	
q‴q = (012) (011)........	5	15 56—16 21	16 11	16 7	4	
cq = (001) (011)........	28	36 13—36 26	36 18	36 14	4	36 21
qq′ = (011) (021)........	13	19 21—19 41	19 26	19 28	2	19 30
q′b = (021) (010)........	14	33 59—34 25	34 15	34 18	3	
q′q″ = (021) (031)........	—	—	—	9 50	—	
q″b = (031) (010)........	—	—	—	24 28	—	
qb = (011) (010)........	27	53 32—53 52	53 42	53 46	4	53 48
ao = (100) : (111)........	—	—	—	43 13	—	
oq = (111) : (011)........	45	46 36—46 55	46 47	*	—	46 50
oo = (111) : (1Ī1)........	20	86 14—86 40	86 26	86 26	0	
ao′ = (100) : (112)........	—	—	—	58 14	—	
o′o′ = (112) : (1Ī2)........	—	—	—	63 32	—	
bo = (010) : (111)........	51	65 53—66 19	66 6	66 7	1	66 11
oo = (111) : (1Ī1)........	8	47 35—47 50	47 42	47 46	4	47 48
bo′ = (010) : (112)........	—	—	—	73 0	—	
o′o′ = (112) : (1Ī2)........	—	—	—	84 0	—	
co′ = (001) : (112)........	2	36 54—37 9	37 2	37 2	0	
o′o = (112) : (111)........	2	19 16—19 28	19 22	19 26	4	
co = (001) : (111)........	50	56 12—56 41	56 28	*	—	56 29
op = (111) : (110)........	33	33 11—33 48	33 32	33 32	0	33 40
po = (110) : (1Ī1)........	—	—	—	63 52	—	
oq′ = (1Ī1) : (021)........	—	—	—	49 47	—	
q′p = (021) : (Ī10)........	—	—	—	66 21	—	
po′ = (110) : (1Ī2)........	—	—	—	71 27	—	
o′q = (1Ī2) : (0Ī1)........	—	—	—	35 14	—	
qp = (0Ī1) : (Ī10)........	—	—	—	73 19	—	
p′o = (130) : (111)........	—	—	—	43 47	—	
oo′ = (111) : (1Ī2)........	—	—	—	45 3	—	
o′q′ = (1Ī2) : (021)........	—	—	—	46 16	—	
q′p′ = (021) : (Ī30)........	—	—	—	44 54	—	
p′o′ = (130) : (112)........	—	—	—	58 33	—	
o′q = (112) : (0Ī1)........	—	—	—	61 54	—	
qp′ = (0Ī1) : (Ī30)........	—	—	—	59 33	—	
Total number of measurements }	315					

On the other hand, the faces of the primary prism $p = \{110\}$ were invariably poor, being both distorted and badly reflecting, quite exceptionally so, and this was rendered the more striking by the brilliance and planeness of the other primary faces. In this respect thallium differs remarkably from the sulphates of the alkali metals proper—potassium, rubidium, and cæsium, and from ammonium sulphate. Even when these primary prism faces were quite large, as not unfrequently happened, they were always dull, and distorted, and untrustworthy as regards their reflections. The smaller faces of the prism $p' = \{130\}$ were, likewise, similarly affected by distortion. The mean values of the angles involving these faces, however, the individual values being only the chosen best, agree well with those calculated from the irreproachably determined basal angles oq and co, so that there is no ambiguity as to the positions of the faces in question.

The macropinakoid $a = \{100\}$ was not observed on any of the crystals.

Von Lang also remarked the same elongation parallel to the axis which corresponded in his description with the author's axis a, the tabular development parallel to the brachypinakoid, and the brilliance and adamantine lustre of the faces.

Cleavage.—The investigation of the cleavage directions was a difficult matter, owing to the small size of the crystals. The chief cleavage, a perfect one, is parallel to the tabular plane of the thin plates, namely, the brachypinakoid, $b = \{010\}$. The crystals also cleave parallel to the basal pinakoid $c = \{001\}$, but the cleavage in this direction is not so perfect.

Volume.

Relative Density.—The following four values for the specific gravity at $20°$, compared with that of water at $4°$, were obtained by the author's pyknometer-with-cap method, the Retgers immersion method being unavailable, on account of the specific gravity of the crystals being higher than that of any immersion liquid. Carbon tetrachloride was the liquid employed in the pyknometer, its specific gravity being freshly redetermined. The weight of the exceedingly finely powdered and carefully dried salt used varied from $7·4805$ to $10·4913$ grammes.

Specific Gravity of Tl_2SO_4 at $20°/4°$.—$6·7585$, $6·7646$, $6·7517$, $6·7545$.

The value accepted is $6·765$, the highest of the individual values obtained, as being nearest the truth, any slight error in the pyknometer method results being invariably in the direction of lowness, due to the inclusion of liquid or air cavities in the crystal particles. This was fully discussed and proved in a former memoir.* When an immersion method result for any

* 'Journ. Chem. Soc.,' 1905, vol. 87, p. 1186.

particular salt was available for comparison with that derived by use of the pyknometer, the highest value afforded by the latter was always found to correspond with the value given by the immersion method.

Molecular Volume.— $\dfrac{M}{d} = \dfrac{500\cdot5}{6\cdot765} = 73\cdot98.$

Topic Axes.—These were calculated on the assumption of the same pseudo-hexagonal structure as has been shown to apply to the whole of the salts of the alkali sulphate and selenate series,[*] and which is obviously, owing to the similarity of the angles, equally applicable to thallium sulphate. They are as follows:—

$$\chi : \psi : \omega = 4\cdot0820 : 3\cdot9644 : 5\cdot2299.$$

Optics.

Optical Character.—The directions of the axes of the optical indicatrix are as follows:—Axis a is γ, axis b is β, and axis c is α.

The first median line is the axis a, and the second median line the axis c, so that the plane of the optic axes is the brachypinakoid $b = \{010\}$. These optical characters agree with those given by von Lang, after converting his crystallographic axes into those of the author now generally adopted.

The sign of the double refraction is positive.

Refractive Indices.—Two prisms were eventually obtained which afforded α and β, and β and γ respectively, by the most careful grinding on the author's invaluable orientated-surface-preparing goniometer, after very numerous failures owing to the minute size of the crystals, and their extreme brittleness. The two faces of each prism were symmetrical to an axial plane of the optical ellipsoid and its edge was parallel to an axis of the latter. The usual method of moistening the finely ground glass lap with " brick " oil proved curiously unsuitable, the ground surfaces being afterwards found to be opaque, owing to some exceptional surface action, connected doubtless with the brittleness. But if instead of moistening the lap with oil it were breathed on a few times so as to deposit a close sprinkling of minute drops of water on it, the opacity was not produced, the grinding occurred quickly and steadily, and on finishing with the polishing lap of smooth glass similarly breathed on, an excellent polish was obtained on the miniature facet thus prepared, and a perfect image of the signal slit was afforded by each such surface prepared. The spectra were clearly seen through the minute prisms eventually so obtained, and the refractive indices determined with their aid are given in the next table. The angle of each of the prisms was in the neighbourhood of 50°, as a prism of 60° first prepared did not permit the refracted rays to emerge, owing to the exceptionally high refraction and the occurrence of total internal reflection.

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[*] Memoir just cited, p. 1184.

The results for β with the two prisms were identical to one unit in the fourth decimal place, so that the indices given in the table are absolutely trustworthy. The γ values, moreover, were confirmed by further measurements with three natural prisms, formed in two cases by an excellent face of b (010) and a narrower, but specially brilliant face of q (011), and in the third case by a c (001) and a q (011) face. Such a prism yields two values, one of which is γ, as the direction of the long prism edge, parallel to which one set of vibrations occurs, is that of the axis a. This is the first time that the refractive indices of thallium sulphate have been determined, a fact quite comprehensible in the light of the facts above given, and it will be seen that the refractive power is extraordinarily high.

Refractive Indices of Tl_2SO_4.

α. Vibrations parallel axis c.	β. Vibrations parallel axis b.	γ. Vibrations parallel axis a.
Li......... 1·8493	Li......... 1·8563	Li......... 1·8739
C .... 1·8509	C .... 1·8579	C .... 1·8755
Na ...... 1·8600	Na ...... 1·8671	Na ...... 1·8853
Tl......... 1·8704	Tl......... 1·8778	Tl......... 1·8964
F .... 1·8859	F .... 1·8935	F .... 1·9126

Mean refractive index for Na light (mean of α, β, and γ) = 1·8708.

The intermediate index β is expressed accurately for any wave-length λ, as far as that of the green thallium line in the spectrum, and approximately from thence onwards towards the blue, by the following formula:—

$$\beta = 1·8251 + \frac{1\ 252\ 828}{\lambda^2} + \frac{7\ 606\ 590\ 000\ 000}{\lambda^4} + \dots .$$

The α indices are also afforded by the formula if the constant 1·8251 is diminished by 0·0072, and the γ indices if it is increased by 0·0182.

Axial Ratios of the Optical Ellipsoid.—These constants work out as under:—

Axes of indicatrix .... $a : b : c = \gamma : \beta : \alpha = 1·0097 : 1 : 0·9962$.

Axes of optical velocity ellipsoid ... $c : b : a = 0·9904 : 1 : 1·0038$.

Molecular Optical Constants.—These constants are as follows:—

	Crystallographic axis............ a.	b.	c.
Specific refraction (Lorenz) $\frac{n^2-1}{(n^2+2)d}$ for ray C ...	0·0674	0·0665	0·0661
Molecular refraction (Lorenz) $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$ for ray C ...	33·76	33·27	33·08
Molecular refraction (Gladstone) $\frac{(n-1)M}{d}$ for ray C	64·74	63·47	62·95

Mean molecular refraction (Gladstone) for all three axes, 63·72.

Optic Axial Angle.—After many fruitless attempts two section-plates were eventually obtained perpendicular to the first and second median lines respectively, by grinding, and polishing on a smooth glass lap moistened by breathing on it, as described for the preparation of the prisms. Through the one perpendicular to the first median line, this plate being a section across the elongated prism, the optic axes were invisible in air; they were well out of the field of view, portions of rings being alone visible symmetrically to the centre, on the right and left margins of the field. In bromnaphthalene, however, the axes were clearly visible, and the following values for the apparent optic axial angle, $2Ha$, were obtained for three wave-lengths, which alone gave brushes sufficiently well illuminated for measurement, owing to the small amount of light which so minute a section-plate permits to pass.

Apparent Optic Axial Angle, $2Ha$, *in Br-naphthalene.*

For C light............ $77\overset{\circ}{}\ 50'$

„ Na „ 77 43

„ Tl „ 77 35

The section perpendicular to the second median line was formed by a particularly good natural c (001) face, as usual the elongated narrow side of a prism, and by a second face ground and polished by the moist lap, parallel to it. No trace of the optic figure was visible in air; and in bromnaphthalene, although rings were visible symmetrical to the centre, the axes remained outside the field on each side when the section was rotated to the extreme limits. This is owing to the fact that the refractive index of the crystal (mean for Na 1·8708) is considerably higher than that of the immersion liquid (1·6657 for Na).

The usual method of determining the true optic axial angle, $2Va$, by measurements of $2Ha$ (the apparent acute angle in bromnaphthalene) and $2Ho$ (the apparent obtuse angle in the same liquid), and calculation by the formula tan $Va = \sin Ha/\sin Ho$, thus fails in this case. It was determined, however, from the data afforded by the measured values of $2Ha$, the intermediate refractive index β, and the refractive index n of bromnaphthalene (which was determined for the actual immersion liquid employed), the calculation being made with the aid of the formula :—

$$\sin Va = \frac{n}{\beta} \sin Ha.$$

The refractive indices of the specimen of bromnaphthalene used, supplied by Merck, were found to be as follows, by use of a small hollow 60° prism of glass, with truly plane sides.

Refractive Indices of Bromnaphthalene.

Li, 1·6554; C, 1·6565; Na, 1·6657; Tl, 1·6761; F, 1·6895; G, 1·7123.

The values of the true optic axial angle, $2Va$, obtained in this manner, are as follows:—

True Optic Axial Angle of Tl_2SO_4.

$$
\begin{array}{lcc}
\text{For C light} \dots\dots\dots\dots & \overset{\circ}{68} & \overset{\prime}{8} \\
\text{,, \ Na \ ,,} \dots\dots\dots\dots & 68 & 4 \\
\text{,, \ Tl \ \ ,,} \dots\dots\dots\dots & 68 & 0 \\
\end{array}
$$

The true angle between the optic axes is thus 8′ greater for red C light than it is for green thallium light.

Thallium Selenate, Tl_2SeO_4.

Preparation and Analysis.—A quantity of specially pure carbonate of thallium, supplied by Merck, was employed as the basal material. It was dissolved in small amounts at a time in a considerable volume of water, adequate at the boiling temperature to completely effect solution, and then treated with a slight excess of pure selenic acid, also furnished by Merck. On account of the difficult solubility the solution requires to be kept very dilute; the selenate is, in fact, somewhat less soluble (2 grammes in 100 grammes of water at the ordinary temperature) than the carbonate of thallium (four parts in 100 of water). On cooling, the hot solution deposited the needle-shaped crystals already described in the introduction, and these were several times redissolved and recrystallised from distilled water, in the manner also described, so as to obtain crystals suitable for measurement.

An analysis of a specimen of the crystals, by conversion into the insoluble iodide, TlI, as in the case of thallium sulphate, gave the following results :—1·0181 grammes thallium selenate yielded 1·2250 grammes of TlI, which corresponded to 74·19 per cent. of thallium. The theoretical percentage is 74·04.

Solubility.—Two determinations were carried out for the ordinary and the boiling temperatures. It was found that :—

100 grammes of water at 9°·3 dissolve 2·13 grammes of thallium selenate.

100 ,,   ,,   100°   ,,   10·86   ,,   ,,   ,,

Thallium selenate thus proves to be less soluble than the sulphate, a fact which accounts for the smaller size of the crystals, and their greater tendency to be deposited in minute needles.

Goniometry.

Crystal System.—Orthorhombic, holohedral class.

Habit.—Acicular to elongated prismatic. The faces in the prism zone were more equally developed than in the sulphate, and only occasionally were the long prisms tabular, and then the flat plane was parallel to either $b = \{010\}$, $c = \{001\}$ or $q = \{011\}$.

Ratio of Axes.—$a : b : c = 0.5551 : 1 : 0.7243$.

Forms observed.—$a = \{100\}$, $b = \{010\}$, $c = \{001\}$, $p = \{110\}$, $p' = \{130\}$, $q = \{011\}$, $q' = \{021\}$, $o = \{111\}$.

Crystal Angles.—The results of the measurements with eleven crystals selected from five different crops, and of the calculations, are given in the accompanying table.

The best developed of the crystals measured is illustrated in fig. 3, and is typical of the prisms obtained by the cooling during a night of solutions
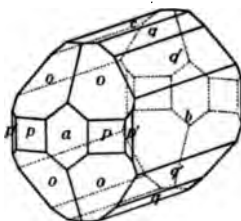
Fig. 3.

containing only slightly more thallium selenate than corresponds to saturation at the ordinary temperature. The prism zone comprises faces more or less equally developed of the brachypinakoid $b = \{010\}$, the two brachyprisms $q = \{011\}$ and $q' = \{021\}$, and the basal pinakoid $c = \{001\}$. The ends are sharpened by the faces of the primary pyramid $o = \{111\}$, and frequently no other end faces at all were observed. Alternate pairs of the o faces were often preponderatingly developed at the two ends, giving to the crystal a hemimorphic appearance. The crystals, however, belong to the holohedral class of the rhombic system, Class 8, and not to either of the two classes, 6 or 7, of lower rhombic symmetry. The other pair of o faces at each end are always present, and the curious habit is generally accompanied by a tabular development parallel to $q = \{011\}$.

An excellent small face of the orthopinakoid $a = \{100\}$ was present on the crystal shown in the drawing, as well as two faces of the primary prism $p = \{110\}$, and two narrower faces of the prism $p'\{130\}$.

The faces of the crystals were very brilliant, and the lustre adamantine, as in the case of the sulphate.

Morphological Angles of Thallium Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
ap = (100) : (110)	1		29 7	29 2	5
pp' = (110) : (130)	—	—	—	29 59	—
ap' = (100) : (130)	—	—	—	59 1	—
$p'b$ = (130) : (010)	1	—	30 54	30 59	5
pb = (110) : (010)	2	60 53—60 59	60 56	60 58	2
cq''' = (001) (012)	—	—	—	19 55	—
$q'''q$ = (012) (011)	—	—	—	16 0	—
cq = (001) (011)	89	35 46—36 4	35 56	35 55	1
qq' = (011) (021)	14	19 16—19 35	19 23	19 28	5
$q'q''$ = (021) (031)	—	—	—	9 54	—
$q''b$ = (031) (010)	—	—	—	24 43	—
cq' = (001) (021)	14	55 2—55 39	55 19	55 23	4
$q'b$ = (021) (010)	18	34 27—34 55	34 41	34 37	4
qb = (011) (010)	24	53 53—54 13	54 4	54 5	1
ao = (100) : (111)	37	43 18—43 35	43 26	43 25	1
oq = (111) : (011)	44	46 20—46 50	46 35	*	—
ao' = (100) : (112)	—	—	—	58 28	—
$o'q'''$ = (112) : (012)	—	—	—	31 32	—
bo = (010) : (111)	40	66 0—66 21	66 12	66 13	1
oo = (111) : (1̄11)	18	47 21—47 42	47 35	47 34	1
bo' = (010) : (112)	—	—	—	73 8	—
$o'o'$ = (112) : (1̄12)	—	—	—	33 44	—
co' = (001) : (112)	—	—	—	36 44	—
$o'o$ = (112) : (111)	—	—	—	19 27	—
co = (001) : (111)	37	56 3—56 22	56 11	*	—
op = (111) : (110)	14	33 33—33 58	33 48	33 49	1
oo = (111) : (11̄1)	17	67 23—67 45	67 37	67 38	1
po = (110) : (1̄11)	—	—	—	63 56	—
oq' = (1̄11) : (0̄21)	—	—	—	49 36	—
$q'p$ = (0̄21) : (1̄10)	—	—	—	66 28	—
po' = (110) : (1̄12)	—	—	—	71 33	—
$o'q$ = (1̄12) : (0̄11)	—	—	—	34 59	—
qp = (0̄11) : (1̄10)	—	—	—	73 28	—
$p'o$ = (130) : (111)	—	—	—	43 59	—
oo' = (111) : (112)	—	—	—	44 51	—
$o'q'$ = (1̄12) : (021)	—	—	—	46 .2	—
oq' = (111) : (021)	—	—	—	90 53	—
$q'p'$ = (021) : (1̄30)	—	—	—	45 8	—
$p'o'$ = (130) : (112)	—	—	—	58 48	—
$o'q$ = (112) : (0̄11)	—	—	—	61 24	—
qp' = (0̄11) : (1̄30)	—	—	—	59 48	—
Total number of measurements }	320				

Cleavage.—The cleavage directions of thallium selenate appear to be identical with those of the sulphate, namely, the brachypinakoid $b = \{010\}$ and the basal pinakoid $c = \{001\}$, although great difficulty was experienced in obtaining satisfactory cleavages, owing to the still smaller size of the selenate crystals.

Volume.

Relative Density.—Four specific gravity determinations by the pyknometer method gave the following results. The Retgers immersion method is here impossible of application on account of the very high specific gravity :—

Specific Gravity at $20°/4'$.—6·8745, 6·8669, 6·8716, 6·8723.

Somewhat over 9 grammes weight of the powdered crystals were employed in each determination. The highest of the values was accepted as the true density, for reasons given in discussing the sulphate, namely, 6·875.

Molecular Volume.—$\dfrac{M}{d} = \dfrac{547·3}{6·875} = 79·61.$

Topic Axes.—These are as follows, calculated for a pseudo-hexagonal structure :—

$$\chi : \psi : \omega = 4·1124 : 4·0763 : 5·3189.$$

Optics.

Optical Character.—The disposition of the axes of the optical ellipsoid (indicatrix) is not the same as in the case of the sulphate, but as follows:—

The axis α is parallel to the crystallographic axis b.

    „ β „   „   „ c.

    „ γ „   „   „ a.

The acute bisectrix of the optic axial angle is the crystallographic axis b, and the obtuse bisectrix is the axis a. Hence the plane of the optic axes is the basal plane $c = \{001\}$.

The double refraction is also different, being negative.

Refractive Indices.—Two complementary 50° prisms (a 60° prism not permitting the whole spectrum to emerge) were eventually, after many failures with such minute crystals, ground symmetrically to an axial plane of the ellipsoid, and with the edge in each case parallel to an axis of the same; and they were polished in the same manner as those of the sulphate. One of them afforded directly α and β, and the other β and γ. The two series of values obtained for β from the two prisms were identical, and the following table represents the results for all three indices.

Refractive Indices of Thallium Selenate.

α. Vibrations parallel axis b.	β. Vibrations parallel axis c.	γ. Vibrations parallel axis a.
Li......... 1·9331	Li......... 1·9426	Li....·.... 1·9476
C .... 1·9355	C .... 1·9450	C .. .. 1·9500
Na ...... 1·9493	Na ...... 1·9592	Na ...... 1·9640
Tl......... 1·9635	Tl......... 1·9737	Tl......... 1·9782
F .... 1·9840	F .... 1·9942	F .... 1·9987

Mean refractive index for Na light (mean of α, β, and γ) = 1·9575.

The intermediate refractive index β is afforded for any wave-length λ by the following formula, as far as the green thallium line in the spectrum, and approximately for wave-lengths beyond towards the blue:—

$$\beta = 1\cdot8755 + \frac{3\ 385\ 187}{\lambda^2} - \frac{16\ 164\ 430\ 000\ 000}{\lambda^4} + \ldots$$

The α indices are also afforded by the formula if the constant 1·8755 is diminished by 0·0099, and the γ values if it is increased by 0·0048.

The negative character of the double refraction is indicated by the closer approximation of the β values to the γ values than to the α values.

Axial Ratios of the Optical Ellipsoid.—

Axes of indicatrix .... $a:b:c = \gamma:\alpha:\theta = 1\cdot0075:1:1\cdot0051.$

Axes of optical velocity ellipsoid ... $\mathfrak{c}:\mathfrak{a}:\mathfrak{b} = 0\cdot9925:1:0\cdot9949.$

Molecular Optical Constants.—

Crystallographic axis............ *a.*   *b.*   *c.*

Specific refraction (Lorenz) $\frac{n^2-1}{(n^2+2)\,d}$ for ray C ...... 0·0703   0·0695   0·0700

Molecular refraction (Lorenz) $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$ for ray C ... 38·45   38·05   38·31

Molecular refraction (Gladstone) $\frac{(n-1)M}{d}$ for ray C 75·63   74·47   75·23

Mean molecular refraction, mean of all three values of $\frac{(n-1)M}{d} = 75\cdot11.$

*Optic Axial Angle.—*A few coloured rings of the optic axial interference figure in convergent polarised light were visible in air, at the margin of the field on each side, through a particularly clear and adequately thick tabular crystal eventually obtained parallel to the brachypinakoid $b = \{010\}$, which is perpendicular to the first median line, but the axes themselves were out of the field on each side. On immersing it in a cell of bromnaphthalene

the optic axes surrounded by their rings and lemniscates were clearly seen, and the following measurements obtained for 2Ha :—

$$C \quad \dots\dots\dots \quad 89°\ 0'$$
$$Na \quad \dots\dots\dots \quad 88\ 45$$
$$F \quad \dots\dots\dots \quad 88\ 20$$

The negative character of the double refraction was confirmed by means of the quarter undulation plate and quartz wedge.

An excellent plate was then ground and polished successfully, after several attempts, perpendicular to the second median line, the axis a. It showed the optic figure well, symmetrical to the centre, but the optic axes were outside the field, even when immersed in bromnaphthalene or methylene iodide. For, owing to the refractive indices being so high, higher than those of the immersion liquids, the angle 2Ho in either would be considerably larger than the true obtuse angle within the crystal, and as this is 107°, the angle would probably be too large to emerge. Such, indeed, appears to be the case. Hence the true angle 2Va was found from the measured values of 2Ha in bromnaphthalene, combined with the specially determined refractive indices n of that liquid for the same wave-lengths, and the β refractive indices of the crystal already determined, employing the formula

$$\sin V a = \frac{n}{\beta} \sin H a.$$

The values thus obtained for 2Va were as under :—

True Optic Axial Angle of Thallium Selenate.

$$\text{For C light} \dots\dots\dots \quad 73°\ 18'$$
$$\text{,, Na ,,} \quad \dots\dots\dots \quad 72\ 58$$
$$\text{,, F ,,} \quad \dots\dots\dots \quad 72\ 22$$

Discussion of Results.

Solubility.—A comparison of the degrees of solubility in water of the ten salts of the series now fully investigated is afforded by the following table, which represents the number of grammes of the respective salts which are dissolved by 100 grammes of water at 12° :—

Solubility in Water at 12°.

K_2SO_4	10·0	K_2SeO_4	115·0
Rb_2SO_4	42·0	Rb_2SeO_4	159·0
Cs_2SO_4	160·0	Cs_2SeO_4	245·0
$(NH_4)_2SO_4$	74·0	$(NH_4)_2SeO_4$	122·0
Tl_2SO_4	4·3	Tl_2SeO_4	2·4

It is thus obvious that the thallium salts are the least soluble of the series, and, moreover, that the general rule, according to which the selenate is more soluble than the sulphate, is not followed in the case of the selenate of thallium, indicating some intrinsic difference between thallium on the one hand and the alkali metals proper and ammonium on the other.

Goniometrical Morphology.—The interfacial angles now given for thallium sulphate and selenate are set forth in comparative form in the accompanying table, side by side with those given in the author's former memoirs for the sulphates and selenates of potassium, rubidium, and cæsium, and for ammonium sulphate. Ammonium selenate, the last salt described by the author,* is not comparable on account of its crystallising differently, in the monoclinic instead of the rhombic system. It is at once apparent that although the angles are precisely analogous and sufficiently close to warrant the inclusion of thallium sulphate and selenate in the same " isomorphous " series,—giving the term " isomorphism " the broad signification now assigned to it by the author so as to admit such relatively minute changes of angle as have been shown to accompany, in accordance with a regular law, the replacement of one metal of the same family group by another,—yet that the angular changes introduced by the replacement of potassium by thallium in the sulphate and selenate are considerably greater than those brought about by the replacement of potassium by either rubidium, cæsium, or (in the case of the sulphate) ammonium.

The most concise method of exhibiting the relative magnitudes of the angular changes in the different cases is by means of a table giving the average change in each instance, that is, the arithmetical mean of all the angular differences between the potassium salt, considered as the first member of the series, and the salt in question, or between any other two salts, ignoring sign, that is whether the angle has increased or diminished.

Such a table is appended after the table of angles, and gives also the maximum change in each case.

* 'Journ. Chem. Soc.,' 1906, vol. 89, p. 1059.

Comparative Table of Interfacial Angular magnitudes.

Angle		K_2SO_4	Rb_2SO_4	Cs_2SO_4	$(NH_4)_2SO_4$	Tl_2SO_4	K_2SeO_4	Rb_2SeO_4	Cs_2SeO_4	Tl_2SeO_4
ap	$=(100):(110)$	29 48	29 47	29 44	29 24	29 3	29 49	29 43	29 41	29 2
pp'	$=(110):(130)$	30 0	30 0	30 0	30 0	29 59	30 0	30 0	30 0	29 59
$p'b$	$=(130):(010)$	30 12	30 13	30 16	30 36	30 58	30 11	30 17	30 19	30 59
cq''	$=(001):(012)$	20 21	20 31	20 38	20 6	20 7	20 6	20 16	20 22	19 55
$q''q$	$=(012):(011)$	16 13	16 18	16 21	16 6	16 7	16 6	16 11	16 13	16 0
cq	$=(001):(011)$	36 34	36 49	36 59	36 12	36 14	36 12	36 27	36 36	35 55
qq'	$=(011):(021)$	19 27	19 26	19 26	19 28	19 28	19 28	19 27	19 26	19 28
$q'q''$	$=(021):(031)$	9 47	9 45	9 42	9 51	9 50	9 51	9 49	9 47	9 54
$q''b$	$=(031):(010)$	24 12	24 0	23 53	24 29	24 28	24 29	24 17	24 11	24 43
$q'b$	$=(021):(010)$	33 59	33 45	33 35	34 20	34 18	34 20	34 6	33 58	34 37
ao	$=(100):(111)$	43 52	43 41	43 31	43 39	43 13	44 9	43 51	43 43	43 25
oq	$=(111):(011)$	46 8	46 19	46 29	46 21	46 47	45 51	46 9	46 17	46 35
ad'	$=(100):(112)$	56 44	58 31	58 19	58 37	58 14	59 3	58 45	58 35	58 28
$o'o'$	$=(112):(112)$	62 32	62 58	63 22	62 46	63 32	61 54	62 30	62 50	63 4
bo	$=(010):(111)$	65 37	65 33	65 32	65 56	66 7	65 43	65 42	65 40	60 13
oo	$=(111):(111)$	48 46	48 54	48 56	43 8	47 46	48 34	48 36	48 40	47 34
bo'	$=(010):(112)$	72 42	72 37	72 33	72 56	73 0	72 51	72 47	72 43	73 8
$o'o'$	$=(112):(112)$	34 36	34 46	34 54	34 8	34 0	34 18	34 26	34 34	33 44
co'	$=(001):(112)$	36 44	37 0	37 18	36 42	37 2	36 21	36 41	36 52	36 44
$o'o$	$=(112):(111)$	19 27	19 26	19 25	19 27	19 26	19 28	19 27	19 26	19 27
co	$=(001):(111)$	56 11	56 26	56 38	56 9	56 28	55 49	56 8	56 18	56 11
oo''	$=(111):(332)$	9 45	9 42	9 40	9 46	9 42	9 49	9 46	9 44	9 45
$o''p$	$=(332):(110)$	24 4	23 52	23 42	24 5	23 50	24 22	24 6	23 58	24 4
op	$=(111):(110)$	33 49	33 34	33 22	33 51	33 32	34 11	33 52	33 42	33 49
po	$=(110):(111)$	65 8	65 2	64 54	64 31	63 52	65 17	65 1	64 55	63 56
oq'	$=(111):(021)$	49 12	49 23	49 30	49 24	49 47	48 57	49 13	49 20	49 36
$q'p$	$=(021):(110)$	65 40	65 36	65 36	66 5	66 21	65 46	65 46	65 45	66 23
po'	$=(110):(112)$	72 23	72 15	72 7	71 58	71 27	72 34	72 19	72 12	71 33
$o'q$	$=(112):(011)$	34 50	35 4	35 15	34 53	35 14	34 31	34 49	34 58	34 59
qp	$=(011):(110)$	72 47	72 41	72 38	73 9	73 19	72 55	72 52	72 50	73 28
$p'o$	$=(130):(111)$	43 59	43 49	43 40	44 0	43 47	44 14	44 1	43 54	43 59
oo'	$=(111):(112)$	45 47	45 55	46 1	45 16	45 3	45 33	45 39	45 43	44 51
$o'q'$	$=(112):(021)$	46 1	46 12	46 20	46 1	46 16	46 46	46 59	46 6	46 2
$q'p'$	$=(021):(130)$	44 13	44 4	43 59	44 43	44 54	44 27	44 21	44 17	45 8
$p'o'$	$=(130):(112)$	58 48	58 35	58 25	58 50	58 33	59 6	58 51	58 42	58 48
$o'q$	$=(112):(011)$	62 12	62 36	62 53	61 43	61 54	61 36	62 1	62 16	61 24
qp'	$=(011):(130)$	59 0	58 49	58 42	59 27	59 33	59 18	59 8	59 2	59 48

Average and Maximum Angular Changes.

Salts compared.	For replacement of :	Average change.		Maximum change.	
K_2SO_4 and Rb_2SO_4	K in K_2SO_4 by rubidium	0	9	0	24
K_2SO_4 and $(NH_4)_2SO_4$ ...	„ ammonium.........	0	14	0	37
K_2SO_4 and Cs_2SO_4	„ cæsium	0	16	0	41
K_2SO_4 and Tl_2SO_4	„ thallium............	0	26	0	76
$(NH_4)_2SO_4$ and Tl_2SO_4 ...	NH_4 in $(NH_4)_2SO_4$ by thallium...	0	14	0	39
Rb_2SO_4 and Tl_2SO_4	Rb in Rb_2SO_4 by thallium	0	25	0	70
Cs_2SO_4 and Tl_2SO_4	Cs in Cs_2SO_4 by thallium	0	27	0	62
Rb_2SO_4 and $(NH_4)_2SO_4$ ...	Rb in Rb_2SO_4 by ammonium......	0	20	0	53
Cs_2SO_4 and $(NH_4)_2SO_4$ ...	Cs in Cs_2SO_4 by ammonium	0	25	0	70
K_2SeO_4 and Rb_2SeO_4	K in K_2SeO_4 by rubidium	0	11	0	36
K_2SeO_4 and Cs_2SeO_4	„ cæsium	0	17	0	56
K_2SeO_4 and Tl_2SeO_4	„ thallium	0	27	0	81
Rb_2SeO_4 and Tl_2SeO_4	Rb in Rb_2SeO_4 by thallium	0	26	0	65
Cs_2SeO_4 and Tl_2SeO_4	Cs in Cs_2SeO_4 by thallium	0	27	0	66

It will be clear from this very instructive table that the average and maximum changes are both one and a-half times as much when thallium replaces potassium as when cæsium replaces potassium in either sulphate or selenate, and three times as much in the sulphate series, or two and a-half times in the selenate series, as when rubidium replaces potassium. They are also twice as much when thallium replaces potassium in the sulphate as when ammonium replaces potassium. In short, the changes introduced by the introduction of thallium are nearly twice as great as the maximum changes introduced by interchanges of the true alkali metals among themselves in the salts of the series.

The actual average amounts of angular change for the replacement of potassium by cæsium and by thallium respectively are 16' and 26' in the sulphate group, and 17' and 27' in the selenate group. The atomic weights of cæsium and thallium being 131·9 and 202·6 respectively, if we calculate what change a metal of atomic weight 202·6 should produce when a metal of 131·9 atomic weight produces 16' or 17', we find it to be 25' and 26' respectively, only 1' from the observed amounts of change on the introduction of thallium into potassium sulphate or selenate instead of potassium. The average amount of angular change produced by the introduction of thallium is thus proportional to its atomic weight, but it is important to note that the directions of the individual changes thus averaged are irregular, that is, their signs are not always the same as those of the regular progressive changes of similar sign which accompany the replacement of potassium by rubidium or cæsium. It is this fact which causes the average changes for the introduction

of thallium into either a potassium, a rubidium, or a cæsium salt to be about equal.

The difference of angle between the sulphate and the selenate of thallium is relatively very small, as is also the case with respect to analogous salts of the two acids containing, respectively, potassium, rubidium, or cæsium. The average change of angle occurring when the sulphur in thallium sulphate is replaced by selenium is 11′, and the maximum change is 30′.

There appears, on the whole, to be most resemblance between the thallium and ammonium salt in the case of the sulphates, the only salts comparable, as will be seen from the fact that the average change for the replacement of ammonium by thallium is only 14′, while for the replacement of either potassium, rubidium, or cæsium by thallium it is about twice as much. In certain zones, however, there was also a close similarity of angle between the thallium and the rubidium salts of both acids, but the differences in other zones brought the average up to that given in the table. In this connection it is of interest to recall a statement of Muthmann in the year 1894,[*] at the time that the author was in the midst of the work on the sulphates of the alkalies proper, a fact of which Dr. Muthmann was aware:—" Wenn Herr Tutton das Rubidiumsulfat mit dem Thalliumsulfat vergleichen wird, so wird er höchstwahrscheinlich eine ausserordentliche Winkelähnlichkeit der beiden Körper constatiren können, die ihre Erklärung findet in dem geringen Unterschied der Volumina, mit denen die Atome beider Elemente in die Verbindung eintreten." While this turns out not to be strictly the case, except in so far that the whole of the differences under consideration are extremely small, and that the sulphate of thallium is more like the ammonium salt as regards the magnitudes of its angles, still it will be presently shown that all three salts, the sulphates of ammonium, rubidium, and thallium, as well as the selenates of the two latter, are almost identical as regards their structural dimensions in space, which are dependent on certain fundamental angles, which determine the axial ratios, as well as on the molecular volume.

It cannot be too clearly pointed out, however, that only in the cases of the replacement of potassium by rubidium and by cæsium do the changes of angle occur *in the same direction*, according to a regular law of progression, namely, that law which is undoubtedly the main result of the author's work on the series, that *the changes are a function of the atomic weight of the replacing strictly analogous metal.* It is only the three homologous members of the same exclusive family group, potassium, rubidium, and cæsium, which obey this interesting law, the angular changes when ammonium and thallium are the replacing bases occurring irregularly, in both directions.

[*] ' Zeitschr. für Kryst.,' vol. 22, p. 547.

Structural Constants.—In the next table are compared the densities, molecular volumes, crystallographic axial ratios, and topic axial ratios of the two thallium salts with those of the other salts of the series. The topic axial ratios are obtained by the combination of the crystallographic axial ratios with the molecular volume, the formulæ representing the values of χ, ψ, and ω having been repeatedly given in the author's memoirs.[*]

Comparative Values of Structural Constants.

Salt.	Density at 20°/4°.	Molecular weight.	Molecular volume.	Axial ratios. $a : b : c.$	Topic axial ratios. $\chi : \psi : \omega.$
K_2SO_4	2·666	173·04	64·91	0·5727 : 1 : 0·7418	3·8810 : 3·8574 : 4·9964
Rb_2SO_4	3·615	265·14	73·34	0·5723 : 1 : 0·7485	4·0304 : 4·0039 : 5·2366
Cs_2SO_4	4·246	359·14	84·58	0·5712 : 1 : 0·7531	4·2187 : 4·1849 : 5·5175
Tl_2SO_4	6·765	500·50	73·98	0·5555 : 1 : 0·7328	4·0820 : 3·9644 : 5·2299
$(NH_4)_2SO_4$ ...	1·772	131·20	74·04	0·5635 : 1 : 0·7319	4·0792 : 4·0051 : 5·2020
K_2SeO_4	3·067	219·82	71·67	0·5731 : 1 : 0·7319	4·0291 : 4·0068 : 5·1171
Rb_2SeO_4	3·902	311·92	79·94	0·5708 : 1 : 0·7386	4·1672 : 4·1315 : 5·3461
Cs_2SeO_4	4·456	405·92	91·09	0·5700 : 1 : 0·7424	4·3457 : 4·3040 : 5·6058
Tl_2SeO_4	6·875	547·30	79·61	0·5551 : 1 : 0·7243	4·1124 : 4·0763 : 5·3189
$(NH_4)_2SeO_4$	2·194	177·98	81·12	Not comparable	4·5939 : 4·2968 : 5·1506[*]

[*] The topic axes of monoclinic ammonium selenate were calculated on the assumption of a similar pseudo-hexagonal structure to that of the nine rhombic salts. Such a structure is strikingly evident as regards the prism zone, the angles of the prism faces being 59° 38′ and 30° 0′, the prism zone thus resembling the well-known pseudo-hexagonal prism zone of the nine rhombic salts to a remarkable degree, considering the change of system.

A study of the above table reveals the following facts:—

The *axial ratios* of the two thallium salts are somewhat lower than those of the potassium, rubidium, and cæsium salts, but still extraordinarily close to them, considering the chemical difference of thallium from the three alkali metals proper, belonging, as it does, to a different family group of the periodic system. Moreover, in the only case in which a strict comparison with an ammonium salt can be made, that of the sulphate series, the ratios of the thallium salt approximate still more closely to those of the ammonium salt. It may, therefore, with certainty be said, as regards the ratios of the axes of the thallium salts, as was said equally truly of the interfacial angles, that they are such as fully justify us in including thallium sulphate and selenate in the same isomorphous orthorhombic series as the sulphates and selenates of potassium, rubidium and cæsium and the sulphate of ammonium, employing the term isomorphous in the sense which has been defined on p. 366.

But the most striking fact indicated by the table is that the *molecular volumes*

and *topic axial ratios* of the thallium salts are almost identical with those of the rubidium salts, and also with those of the ammonium salts (completely as regards the sulphate, and in the case of ammonium selenate as far as that monoclinic salt is comparable). It would thus appear that structurally thallium takes a place in the series not far removed from rubidium, as has also been shown to be the case with ammonium. This fact is of significance in two senses. Firstly, it demonstrates that the law of progression of the crystal properties, morphological, optical, thermal, and physical in general, according to the atomic weights of the interchangeable elements, such as has been proved to operate in the cases of the potassium, rubidium, and cæsium sulphates and selenates, only applies to strictly homologous isomorphous salts, such as those of the three metals just mentioned, whose interchangeable elements belong to the same exclusive family group of the periodic classification. For otherwise the thallium salts ought to exhibit higher molecular volumes and larger topic axes than the cæsium salts, the atomic weight of thallium being so much higher.

Secondly, the rigid law of progression being no longer operative, as thallium does not belong to the family group of the alkalies proper, but is a sort of hybrid, having relations both with the alkalies and with the lead group, the changes produced are shown to be of a less regular character, and just as the interfacial angular differences occurred on both sides of the regular order of change for family analogues, within limits consistent with the author's definition of an isomorphous series,* so the structural dimensions do not show any relation to the atomic weight of the metal, but are only of necessity such as bring the crystal within the scope of isomorphism, and as a matter of fact they fall about midway in the series, as do those of the ammonium salts. It is scarcely conceivable, however, that the two and a-half times heavier atom of thallium can be introduced without occupying more space than did the lighter atom of rubidium, and the fact that no appreciable difference is apparent in the structural dimensions would appear to confirm the author's conclusion regarding the still more remarkable case of the introduction of the five atoms of the NH_4 group, instead of each atom of rubidium, namely, that the packing of the material part of the atoms or of their spheres of influence is not an absolutely close one, as is assumed in the conception of Pope and Barlow, shortly to be referred to, but that there are intermolecular and interatomic interspaces affording room for such insertions of additional matter.

A possible alternative to the latter supposition is to conclude that the thallium and ammonium salts are not truly isomorphous with those of potassium,

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* *Vide* last paragraph of this memoir.

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rubidium, and cæsium, and therefore that the molecular volumes and topic axes are not strictly comparable. This view, however, is strongly opposed to the evidence of the great bulk of the author's now accumulated facts, and is conclusively negatived by the interesting and important results of the researches of Barker,[*] on the regular growth of soluble salts on each other. Barker has shown that the perchlorates, like the permanganates investigated in 1894 by Muthmann,[†] of rubidium, ammonium, and thallium, possess almost identical molecular volumes and topic axes, just like the analogous sulphates and selenates, and that only such substances as possess similar molecular volumes and topic axes exhibit the property of forming parallel growths. A beautiful and interesting case is that of the parallel growths of sodium nitrate which readily form on calcite, two substances possessing similar rhombohedral crystalline forms, molecular volumes, and topic axial ratios.

It is difficult to see how the production of such parallel growths can be favoured by the similarity of these constants, if the latter are not strictly comparable, for it is precisely their very compatibility, congruency (near equality of the absolute lengths) as regards topic axial ratios, and therefore strict comparability, which induces the growth of one on the other.

The author has shown,[‡] moreover, that rubidium and ammonium selenates crystallise together in large and very perfect rhombic crystals, and that these mixed crystals may contain more than 60 per cent. of the latter salt, although the common form of dimorphous ammonium selenate is monoclinic. The fact is due to the nearness to identity of the structural dimensions of rubidium and ammonium salts, as indicated by the closeness of the molecular volumes and topic axial ratios, for instance, those of rhombic ammonium and rubidium sulphates. If rhombic crystals could be isolated of pure ammonium selenate, it is probable that their molecular volumes and topic axial ratios would be even closer to those of rubidium selenate than are the values for the monoclinic variety given in the table. Great difference of these constants is undoubtedly unfavourable to the formation of mixed crystals, while close approximation is highly favourable.

Wulff[§] has shown that of the three salts K_2SO_4, $(NH_4)_2SO_4$, and Cs_2SO_4, the first and third do not form mixed crystals, the difference of molecular volume being 19·67, while ammonium and potassium sulphates, which only differ by 9·13, and ammonium and cæsium sulphates, which differ by 10·54, do, although the mixed crystals are not often transparent, the difference of

* 'Min. Mag.,' 1907, vol. 14, p. 235 ; and 'Journ. Chem. Soc.,' 1906, vol. 89, p. 1120.

† Loc. cit.

‡ 'Journ. Chem. Soc.,' 1906, vol. 89, p. 1062.

§ 'Zeitschr. für Kryst.,' 1906, vol. 42, p. 558.

volume being still considerable. On the other hand, he obtained, with the greatest ease, large and beautifully transparent homogeneous mixed crystals of ammonium and rubidium sulphates, whose volumes only differ by 0·7.

Gossner* shows, still more recently, that mixed crystals are probably true homogeneous structures, and not mere mechanical mixtures, a result which had also been indicated by the optical measurements of Wulff, and that it may now be accepted as a well-proved fact that only those members of isomorphous series form mixed crystals whose molecular volumes are fairly close together; and he explains it on the assumption that the force of crystallisation brings about actual equalisation of the molecular volumes, one constituent contracting and the other expanding in the act of crystallising together, the amount of such change of volume being only of the same order as that actually observed by the author† (Tutton) to occur in the thermal expansion of the sulphates of potassium, rubidium, and cæsium. Whether this be the true explanation, or whether it is merely a question of mechanical congruency of structural dimensions (the topic axial ratios) within certain limits, which must obviously be narrow, it is absolutely certain that closeness of molecular volume and congruency of topic axes are the conditions for the ready formation of mixed crystals, just as they also are for the production of parallel growths.

All these facts, obtained by four independent observers, unite in indicating that the molecular volumes and topic axial ratios of rubidium, ammonium, and thallium salts are strictly comparable, and, therefore, that the spacial dimensions of their structural units, the molecular unit-parallelopipeda of the space-lattices, are almost identical.

It was in connection with Muthmann's 1894 researches already alluded to, on structural dimensions, including those of the permanganates of the alkalies, that he suggested for them the term "topic axial ratios," from τόπος, "space." Such an expression of the structural dimensions of crystals was already being independently employed by the author at that time under the name of "distance ratios," the formulæ expressing them being identical. A memoir embodying the author's results was published in the same year (1894), so that in this case, as with so many new ideas which prove to be a distinct step forward, the credit is due to two independent workers. Moreover, the idea really originated with Professor Becke, of Prague; but Professor Muthmann and the author simultaneously applied the idea and showed its practical utility. For the sake of uniformity, the author adopted Muthmann's term, although the ratios really represent the relative distances apart of the centres

* 'Zeitschr. für Kryst.,' 1907, vol. 43, p. 130.

† 'Phil. Trans.,' 1899, A, vol. 192, p. 455.

of gravity of contiguous structural units (in all cases investigated by the author these are the chemical molecules) in the directions of the crystallographic axes, rather than the axial dimensions of the molecule. For we do not yet know the relations of the free space and the actual matter in the unit cell, or elementary parallelopipedon of the space-lattice, corresponding to each molecule. This question of the genesis of " topic axial ratios " is of some moment, for their employment to exhibit the structural relationships of the intimately related members of isomorphous series, with respect to which related substances they are all-sufficient for the purpose, has proved so instructive that the idea has been carried further by Pope and Barlow[*] in an attempt to connect the structure of dissimilar substances.

The essence of their conception, as the author understands it, is that the chemical molecule may be considered as made up of a number of spheres corresponding to and representing the spheres of influence of the atoms composing it; that the volume of each sphere is roughly proportional to the valency of the atom which it represents; and that the sum of the valencies of the atoms present in the molecule may be substituted for the molecular volume, and is termed by them the " valency volume." By using the valency volume instead of the molecular volume in the author's formulæ for calculating the topic axial ratios, they arrive at new ratios, which they term " equivalence parameters." By the use of these they have accounted for the crystalline structure of a number of substances connected morphotropically, and others still less intimately connected. The author hopes to see further developments of these interesting speculations, but, meanwhile, a word must be said as to a very misleading statement in the paper by Pope and Barlow, which reads (p. 1680):—

" The topic axial ratios have no signification which assists in the detection of relationships between crystalline form and molecular constitution, and it is for this reason that their study has hitherto afforded no information on the subject which could not have been equally well derived from the consideration of the ordinary axial ratios." It has been abundantly proved in the author's previous memoirs, and will be particularly clear from the present one, that within an isomorphous series, such as that now under consideration and the monoclinic series of double salts dealt with in former papers, the teaching of topic axial ratios is of paramount importance as regards the structural relationships of the various members of the series, and has assisted materially in the discovery of the law of progression according to atomic weight in the case of the more strictly eutropic members of such series, by showing that such a law is valid for the structural relationships, although the law is indepen-

* 'Journ. Chem. Soc.,' 1906, p. 1675.

dently proved by the relationships with respect to every other property. The ratios of the axes do not show these relationships, as the author has frequently pointed out. Neither are the crystallographic axial ratios of any use as indicative of the possibility or otherwise of the formation of mixed crystals or parallel growths, whereas the great importance of topic axial ratios in this respect has been clearly shown. Moreover, the equivalence parameters of Pope and Barlow, although they may, and the author hopes they will, prove of great value in the connection of dissimilar substances, do not make clear the relationships in an isomorphous series, for they are, from their very nature, almost identical for all the members of an isomorphous series. Further, topic axial ratios depend on a constant determinable with great accuracy, the molecular volume; it is the quotient of the two most accurately determined of all constants, the molecular weight (sum of the atomic weights) and the specific gravity; whereas, at the best, the valency volume is only a rough approximation, although it may prove none the less useful when used for its legitimate purpose.

Topic axes were designed by the author solely for use in isomorphous series, where we could be reasonably sure that the structure, whatever it was, was similar for all the members of the series. Whilst the molecular volume represents the total relative change of volume on passing from one member to another, the topic axial ratios give the directional changes in the separation of the structural units, the chemical molecules, in the three directions of space. The structural unit might even be the complex physical molecule, which Wyrouboff, in his *particule crystalline*, still insists on,[*] although the author has clearly proved in the paper on "The Nature of the Structural Unit"[†] that in the isomorphous series in question the simple chemical molecule itself is the structural unit (a fact which M. Wyrouboff appears to have overlooked). The possibility of a complex unit would not diminish in the slightest degree the value of the teaching of topic axial ratios, for the unit would be the same for all the members of the series, and the relationships would hold equally well, whatever it might be.

Enough will have been said to prove that topic axial ratios are undoubtedly the most suitable constants for comparing the structural dimensions of the members of isomorphous series, and if the equivalence parameters of Pope and Barlow prove as useful in regard to the structural relationships of less intimately connected substances, great progress will have been made.

Cleavage.—Thallium sulphate and selenate both cleave perfectly parallel to the brachypinakoid $b = \{010\}$, and somewhat less perfectly parallel to the

[*] 'Bull. Soc. Min.,' 1906, vol. 29, pp. 335 and 354.
[†] 'Journ. Chem. Soc.,' 1896, vol. 69. p. 507.

basal pinakoid c = {001}. These cleavage directions, as well as the relative degrees of facility of cleavage along them, are identical with those developed by the sulphates and selenates of potassium, rubidium, and caesium. Ammonium sulphate shows the second cleavage as a perfect one, but none in the direction of the brachypinakoid.

Optical Characters.—A very remarkable fact as regards the optics of this series is the diversity of optical character developed. The potassium and caesium salts have opposite characters, and the rubidium salts fall somewhere intermediate in optical character, the progression in the dimensions of the optical ellipsoid according to the atomic weight of the alkali metal having, in fact, been shown to be the cause of the diversity. Still more permutations of optical character are introduced with the advent of ammonium and thallium, but no regular law governing them is now apparent. Thallium and ammonium both resemble the rubidium salt in the case of the sulphate series, but thallium selenate resembles caesium selenate instead. A general survey of the optical characters is taken in the next table, which will render these facts clearer.

Table of Optical Characters.

Salt.	Plane of optic axes.	Direction of first median line.	Sign of double refraction.	Optical scheme.
K₂SO₄	a = (100)	axis c	+	b a c +
Rb₂SO₄ (at 50°—180°) ...	b = (010)	„ a	+	c b a +
(NH₄)₂SO₄	b = (010)	„ a	+	c b a +
Tl₂SO₄.....................	b = (010)	„ a	+	c b a +
Cs₂SO₄	b = (010)	„ c	—	c b a
K₂SeO₄	a = (100)	„ c	+	b a c +
Rb₂SeO₄	a = (100)	„ c	+	b a c +
Tl₂SeO₄	c = (001)	„ b	—	c a b
Cs₂SeO₄	c = (001)	„ b	—	c a b

Refractive Indices.—These are compared for all the nine salts of the series in the next table.

Comparative Table of Refractive Indices.

Crystal axis	Light	K₂SO₄	Rb₂SO₄	Am₂SO₄	Cs₂SO₄	Tl₂SO₄	K₂SeO₄	Rb₂SeO₄	Am₂SeO₄	Cs₂SeO₄	Tl₂SeO₄
a	Li	1·4924	1·5120	1·5297	1·5683	1·8789	1·5357	1·5504	1·5798*	1·5964	1·9476
	C	1·4928	1·5124	1·5302	1·5687	1·8755	1·5362	1·5509	1·5806*	1·5989	1·9500
	Na	1·4947	1·5144	1·5330	1·5662	1·8853	1·5390	1·5537	1·5846*	1·6003	1·9840
	Tl	1·4967	1·5166	1·5359	1·5690	1·8964	1·5421	1·5570	1·5885*	1·6038	1·9782
	F	1·4995	1·5194	1·5394	1·5725	1·9128	1·5460	1·5609	1·5935*	1·6084	1·9987
	G	1·5024	1·5235	1·5445	1·5775	—	1·5517	1·5668	1·6005*	1·6152	
b	Li	1·4912	1·5108	1·5199	1·5615	1·8568	1·5320	1·5482	1·5561	1·5950	1·9331
	C	1·4916	1·5112	1·5204	1·5619	1·8579	1·5325	1·5487	1·5571	1·5965	1·9355
	Na	1·4935	1·5181	1·5280	1·5644	1·8671	1·5352	1·5515	1·5607	1·5989	1·9493
	Tl	1·4955	1·5153	1·5258	1·5672	1·8778	1·5383	1·5547	1·5641	1·6024	1·9635
	F	1·4982	1·5181	1·5291	1·5706	1·8935	1·5421	1·5586	1·5687	1·6070	1·9840
	G	1·5012	1·5222	1·5340	1·5756	—	1·5478	1·5646	1·5752	1·6188	
c	Li	1·4950	1·5109	1·5177	1·5569	1·8498	1·5418	1·5549	1·5584*	1·5990	1·9426
	C	1·4954	1·5113	1·5182	1·5573	1·8509	1·5418	1·5554	1·5594*	1·5965	1·9450
	Na	1·4973	1·5133	1·5209	1·5598	1·8600	1·5446	1·5582	1·5630*	1·5999	1·9592
	Tl	1·4994	1·5155	1·5237	1·5624	1·8704	1·5478	1·5615	1·5665*	1·6034	1·9787
	F	1·5023	1·5188	1·5270	1·5660	1·8859	1·5518	1·5655	1·5718*	1·6080	1·9942
	G	1·5052	1·5224	1·5318	1·5705	—	1·5576	1·5715	1·5781*	1·6148	

* The directions corresponding to these γ and β indices of monoclinic ammonium selenate are nearly but not quite those of the rhombic axes a and c; the directions of the axes b of the two systems correspond exactly, so that the α indices are strictly comparable.

The most striking fact of all, however, with respect to the optical properties will at once be apparent from this table of refractive indices, namely, the very exceptionally high refraction of the thallium salts, as compared with the potassium, rubidium, cæsium and ammonium salts. The mean refractive index (mean of all three indices α, β, and γ for Na-light) of each of the 10 salts is given in the next table, which not only affords a concise expression of the comparative refraction, but legitimately includes also the selenate of ammonium, as the directional differences due to the different system in which that salt crystallises are here eliminated.

Mean Refractive Indices.

K₂SO₄	1·4952	184	0·0444		K₂SeO₄	1·5396	149
Rb₂SO₄	1·5136	120	0·0409		Rb₂SeO₄	1·5545	149
(NH₄)₂SO₄	1·5256	379	0·0438		(NH₄)₂SeO₄	1·5694	303
Cs₂SO₄	1·5635	3073	0·0362		Cs₂SeO₄	1·5997	3578
Tl₂SO₄	1·8708		0·0867		Tl₂SeO₄	1·9575	

The extraordinary difference (increase) of refractive power exhibited by the two thallium salts as compared with the other eight salts will be clearly apparent from this last table. It appears to indicate that optically the thallium salts are essentially different to all the other salts of the series. It has been shown, as regards the morphological constants, the molecular volume and the topic axial ratios, that both the thallium salts and ammonium sulphate behave very much like the corresponding rubidium salts; and that optically, both as regards the refractive indices and the molecular optical constants, ammonium sulphate also resembles rubidium sulphate. But here, in the case of thallium, while the morphological constants are like those of the analogous rubidium salts, the optical constants soar far away, so that we are compelled to conclude that there is some fundamental difference, probably connected with the different nature of the thallium atoms. Before, however, this discussion is carried further, it will be particularly interesting to see whether this marked difference is also exhibited by the molecular optical constants, or whether it is only a phenomenon of the refractive index itself. In the following table, therefore, will be found set out the values of the molecular refraction for all 10 salts, calculated both by the formulæ of Lorenz, and of Gladstone and Dale. In the case of monoclinic ammonium selenate only the strictly comparable directions are represented in the table. In the last column is given the mean molecular refraction, that is, the mean of all three values corresponding to the three axial directions a, b, c of each salt, calculated by Gladstone's formula, and this affords the best comparison of all.

Molecular Refraction for Ray C.

Salt.	Lorenz, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$			Gladstone, $\frac{n-1}{d} M$.			Mean.
	a.	*b.*	*c.*	*a.*	*b.*	*c.*	
K_2SO_4	18·87	18·83	18·95	32·01	31·94	32·18	32·04
Rb_2SO_4	22·04	21·99	22·00	37·61	37·52	37·53	37·55
$(NH_4)_2SO_4$	22·89	22·54	22·46	39·29	38·56	38·40	38·75
Cs_2SO_4	27·51	27·44	27·26	47·71	47·56	47·17	47·48
Tl_2SO_4...............	33·76	33·27	33·08	64·74	63·47	62·95	63·72
K_2SeO_4	22·37	22·24	22·56	38·46	38·19	38·86	38·50
Rb_2SeO_4	25·52	25·43	25·71	44·00	43·82	44·36	44·06
$(NH_4)_2SeO_4$	—	26·13	—	—	45·22	—	45·92
Cs_2SeO_4	31·05	30·99	31·03	54·41	54·28	54·37	54·35
Tl_2SeO_4	38·45	38·05	38·31	75·63	74·47	75·23	75·11

From this table it will be clear that the molecular refractions of thallium sulphate and selenate stand out high above those of the other salts, just as do the refractive indices. So that in the case of the thallium salts, unlike that of the ammonium salts, the optical constants do not follow the morphological constants in indicating a position for thallium near to rubidium in the series.

It may be interesting, in conclusion, to compare the axial dimensions of the optical ellipsoid itself, either the indicatrix or its polar reciprocal, the optical velocity ellipsoid, for the 10 salts of the series. They are given below, and all relate to the value of the *b* axis of the analogous potassium salt, which is taken as unity.

Axial Ratios of Optical Velocity Ellipsoids.

K_2SO_4	0·9992 : 1 : 0·9975	K_2SeO_4	0·9975 : 1 : 0·9939
Rb_2SO_4............	0·9862 : 0·9871 : 0·9869	Rb_2SeO_4	0·9881 : 0·9895 : 0·9853
$(NH_4)_2SO_4$	0·9742 : 0·9806 : 0·9820	$(NH_4)_2SeO_4$ ...	0·9837 : 0·9822 : 0·9688
Cs_2SO_4	0·9536 : 0·9547 : 0·9575	Cs_2SeO_4	0·9593 : 0·9602 : 0·9596
Tl_2SO_4............	0·7922 : 0·7999 : 0·8030	Tl_2SeO_4	0·7817 : 0·7876 : 0·7836

The same fact is here again plainly evident, that the thallium salts are optically exceptional. The optical ellipsoid of each of them lies at a considerable distance inside that of the analogous cæsium salt, such distance being far greater than that of the outermost enveloping ellipsoid of the series, that of the potassium salt, thus indicating a far lower velocity of vibration in the light transmitted through the crystals of the thallium salts, apparently owing to the much greater retarding influence of the thallium atoms.

Summary of Conclusions.

It is shown in this communication that the crystals of the sulphate and selenate of thallium resemble those of the sulphates and selenates of potassium, rubidium, and cæsium, and of the sulphate of ammonium adequately closely morphologically to enable them to be classed in the same orthorhombic isomorphous series, the average difference of the corresponding interfacial angles on the analogous potassium and thallium salts being less than half a degree, and the maximum difference of angle only just exceeding a degree. These differences, however, small as they are, amount to nearly twice as much as those between analogous potassium and cæsium salts, and to nearly three times as much as when rubidium replaces potassium. The ratios of the crystallographic axes are also near enough to the ratios for the other salts to warrant the inclusion of the thallium salts in the series, but. again the difference, though small, is greater than between any other of the salts.

The greater average changes which are observed in the angles, irrespective of their direction, when thallium replaces potassium than when any other of the alkali metals is introduced, are proportional to the higher atomic weight of thallium as compared with that of the other three metals. But the changes occur irregularly as regards their direction, being sometimes in the same direction and sometimes in the opposite direction to what is observed on replacing potassium by rubidium and cæsium. The law which the author's former work has revealed, that the changes in the interfacial angles. are progressive functions of the atomic weights of the interchanged metals, only applies consequently to potassium, rubidium, and cæsium, which belong strictly to the same family group of the periodic classification of the elements. The essentially different nature of thallium, related as it is to both the alkali metals and the lead group, is here displayed, just as was that. of ammonium, whose sulphate also exhibited changes of angle irregular in direction. Indeed, the sulphate of thallium most closely resembles that of ammonium in regard to the magnitude of its angles.

The molecular volumes and topic axial ratios (distances apart of the centres. of gravity of contiguous structural units, the chemical molecules, in the directions of space corresponding to the crystal axes), the latter calculated in accordance with the marked pseudo-hexagonal character of the crystals, of thallium sulphate and selenate are almost identical with those of rubidium sulphate and selenate respectively. Ammonium sulphate has also been shown to possess a molecular volume and topic axial ratios almost identical with those of rubidium sulphate, so that rubidium, thallium, and ammonium are very

closely allied in respect to the structural morphology of their sulphates, and the same applies equally to the selenates of the two metals and to ammonium selenate also if the average of its topic axial ratios is considered, so as to eliminate the directional difference introduced by the different (monoclinic) symmetry of that salt.

Thus the chief morphological result of the investigation is that thallium occupies a place in the alkali series alongside rubidium and ammonium, that is, intermediate between potassium and cæsium.

Optically, the thallium salts exhibit remarkable differences from the potassium, rubidium, cæsium, and ammonium salts. The refractive indices are far higher, the amount by which they are higher than those of the cæsium salts being from $4\frac{1}{2}$ to 6 times greater than the amount by which the latter are higher than those of the potassium salts. The dispersion is also very much higher. Not only are these specific constants themselves higher, but the molecular refraction is likewise very much higher, considerably higher than in proportion to the larger atomic weight of thallium.

In the case of ammonium sulphate, it has previously been shown that the optical properties follow the morphological, in assigning a place to ammonium near rubidium in the series, so that the ammonium group NH_4 behaves in this series very much as though it were a true alkali metal, replacing potassium, rubidium, or cæsium without disturbing the structure or the optical character more than when rubidium is interchanged for one of the other two metals. Thallium, however, resembling ammonium in this respect morphologically, does not do so optically, and therein shows its individuality and its essential chemical difference from the true alkali metals, potassium, rubidium, and cæsium.

The solubility in water of the thallium salts is also very exceptional, and in three senses. For not only is the solubility the lowest in the series, being very sparing indeed compared even with the but slightly soluble sulphate of potassium, but it is lower for the selenate than for the sulphate, whereas all the other selenates of the series are much more soluble than the sulphates, and also the solubility increases with rise of atomic weight of the metal, except in the case of thallium, whose atomic weight is the highest, but solubility lowest.

The results of this investigation throw into prominent relief the main generalisation which has sprung from these researches, that in the case of an isomorphous series in the strictest sense, where the interchangeable elements belong to the same family group of the periodic classification of the elements, the whole of the properties of the crystals, morphological, optical, thermal, and physical, in general, are functions of the atomic weights of these

elements. Where we have an element like thallium, which does not belong to the same family group, the law does not apply, although the metal may be, as thallium is, capable of interchanging with the others without altering the crystal-system, and without making angular and structural changes of much greater magnitude than those provoked by the interchange of family analogues. For such a series the term "eutropic," from "εὐτροπή," meaning "a regularly progressive change (regelmässige Änderung)," has been suggested by Linck,[*] and is adopted by the author.

In the light of this research, the author now defines an "isomorphous series" as "one whose members bear some definite chemical analogy and crystallise according to the same system and in the same class of that system, and develop the same forms inclined at angles which only differ by a very few degrees, rarely exceeding[†] 3°"; and an "eutropic series" as "one in which these small angular differences, and also the structural and physical properties of the crystals, obey the law of progression according to the atomic weight of the interchangeable elements which give rise to the series and which belong to the same family group."

Thallium sulphate and selenate and ammonium sulphate belong to the orthorhombic isomorphous series $R_2 \overset{S}{\underset{Se}{}} O_4$, while the sulphates and selenates of potassium, rubidium, and cæsium belong not only to this same isomorphous series but also to the still more exclusive eutropic series within it.

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[*] 'Zeitschr. für Phys. Chem.,' 1896, vol. 19, p. 197.

[†] The maximum difference met with in the rhombic series in question has been shown to be only 1° 21', which occurs between thallium and potassium sulphates in the case of one angle. The maximum difference yet met with in the monoclinic double sulphate and selenate series is 2° 21'.

On the Two Modes of Condensation of Water Vapour on Glass Surfaces, and their Analogy with James Thomson's Curve of Transition from Gas to Liquid.

By Professor FRED. T. TROUTON, F.R.S.

(Received May 1,—Read June 6, 1907.)

Experiments were made, using glass wool as the substance on which the condensation of water vapour was observed, in continuation of work published last year in the 'Proceedings of the Royal Society '* on the condensation of water vapour by wool and cotton.

The apparatus used is similar to that previously employed except for an alteration to enable the material under examination to be raised in temperature for the purpose of drying.

The general arrangement is shown in fig. 1. The cylindrical bulb holds

To
pump
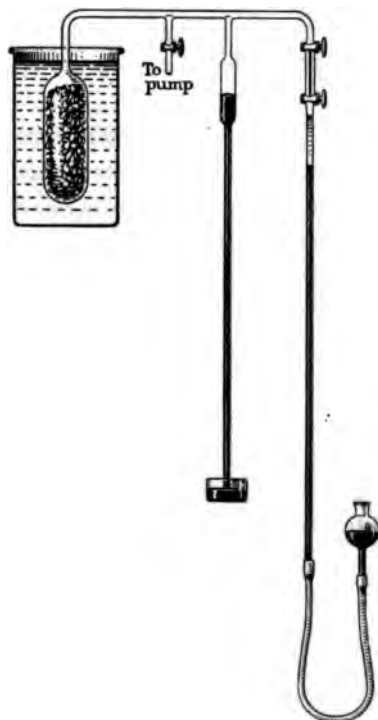
FIG. 1.

the material, and can be surrounded with a vessel of hot oil in order to dry it the more thoroughly. The branch tube on the left leads to the drying

* 'Roy. Soc. Proc.,' A, vol. 77, 1906.

tube and air pump. On the right is the arrangement for supplying known feeds of water freed from air. The volume of the feed is that of the fine bore tube lying between the two taps. Next it is the gauge for reading the vapour pressure.

The glass wool used in these experiments was placed in the bulb seen on the left in the figure, and was dried *in vacuo* at 160° C. for about 70 hours by means of phosphorus pentoxide.

The experiment after that consisted in feeding in water from time to time, and in observing the depression produced in the pressure gauge. The amount of water supplied at each feed was sufficient to saturate the bulb about four times over in the absence of the glass wool.

The character of the curve connecting the pressure with the amount of water held by the glass wool was altogether different from that obtained with wool or cotton. The pressure increases with the quantity of water absorbed much more rapidly at first than with either of those substances; but on reaching a certain critical value the further additions of water reduce the pressure. After that the pressure begins to again increase, with increase of water absorbed, finally passing to saturation in a similar manner to that with wool or cotton.

In making these experiments, several days were allowed to intervene between successive feeds of water, as it was found that some time was required for equilibrium to be set up. In one series of experiments as long as 10 days was given between the feeds, but practically after three days no further change was observed to take place. This was the period allowed in all subsequent experiments.

The following table (p. 385) shows the results obtained in one series of experiments.

The observations in Table I are shown plotted in fig. 2. It will be seen that at about 0·6 cm., or, roughly, at about one-half saturation, a rapid absorption sets in, suggesting a state of supersaturation. The final and initial parts of the curve lie well on the continuous one which has been drawn in as a dotted line. It will be also noticed that, after the breaking down of the stage of supersaturation, a small rise occurs in the actual observation. This has been ignored in drawing the curve, as in amount the variation is almost comparable with the errors of observation; but, on the other hand, similar rises were obtained in the other experiments, suggesting that there may be minute alternations in the pressure following the first breaking down of the state of supersaturation.

It is obvious from these observations that it could be arranged for a glass surface, holding a certain amount of water, to have a less vapour pressure

Table I.

Weight per square centimetre in arbitrary units.	Pressure in centimetres.	Weight per square centimetre in arbitrary units.	Pressure in centimetres.	Weight per square centimetre in arbitrary units.	Pressure in centimetres.
1	0·548	14	1·102	27	1·206
2	0·656	15	1·129	29	1·182
3	0·629	16	1·126	31	1·217
4	0·637	17	1·131	33	1·210
5	0·614	18	1·136	34	1·215
6	0·617	19	1·140	35	1·221
7	0·772	20	1·141	37	1·202
8	0·961	21	1·159	39	1·220
9	1·024	22	1·167	40	1·221
10	1·073	23	1·158	41	1·228
11	1·089	24	1·180	43	1·243
12	1·095	25	1·174	44	1·219
13	1·093	26	1·186	45	1·225

The observed pressures have been reduced to a common temperature of 15° C. by means of the law of isoneres (see 'Roy. Soc. Proc.,' A, vol. 77, 1906, p. 292).
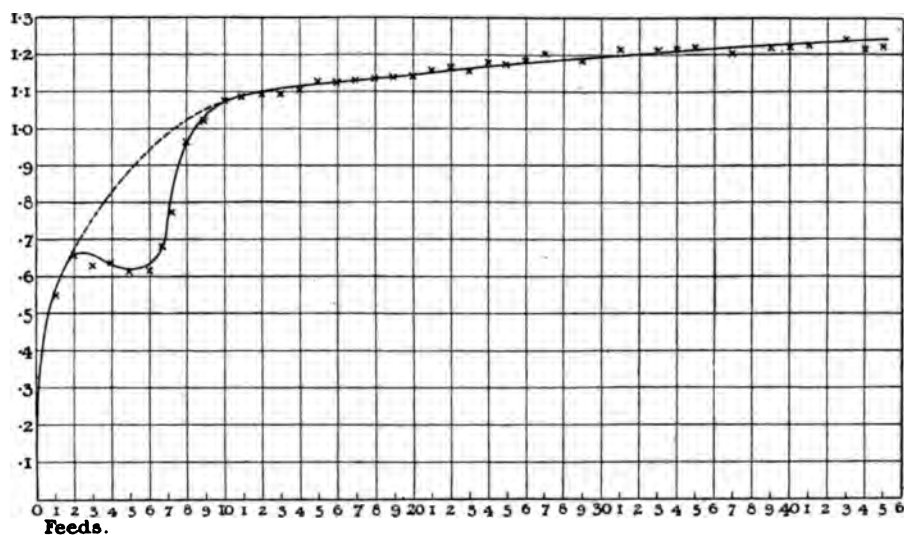
FIG. 2.

than a drier surface, and we are led to the remarkable conclusion that it is quite possible for a relatively wet surface to act as a drying agent to a surface drier than itself.

Two other series of experiments were made, but were only carried as far as the point showing the diminution in pressure on the addition of further moisture. These experiments are shown plotted in figs. 3 and 4.

The supersaturation effect, bringing about this curious diminution in

pressure after a certain point is reached would seem to depend on processes taking place when a gas condenses on a solid, similar in character to those necessary to enable a gas to follow James Thomson's curve of condensation of
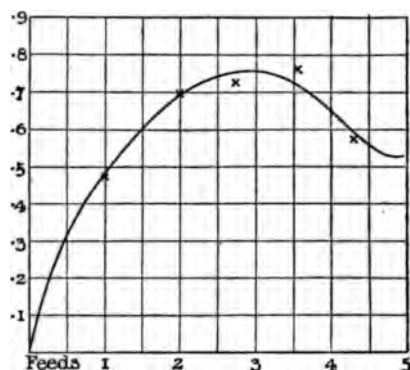
FIG. 3.
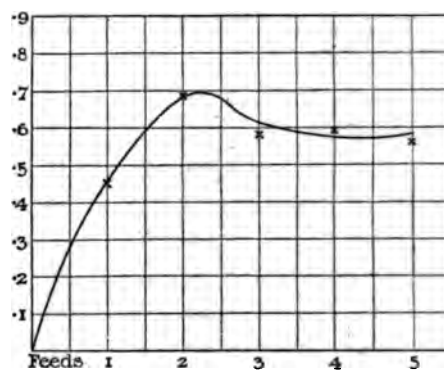
FIG. 4.

vapour to liquid. The isothermal on the pressure-volume curve was conceived by him as passing in a continuous manner from the state of gas to that of liquid (fig. 5). Curves of this kind are given by any of the numerous characteristic gas-equations.
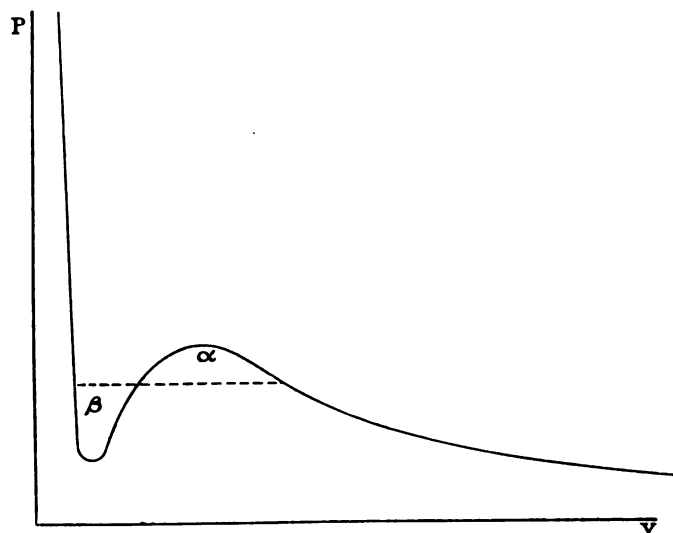
FIG. 5.

That this mode of passage between these states is not one commonly followed is, perhaps, not surprising when we remember that the gas must be enclosed in an envelope in order to be compressed along an isothermal, and

is, on reaching the point a, consequently in contact with material in virtually the liquid state, already deposited on the walls of the containing vessel through surface condensation or absorption at an earlier stage.

In presence of this liquid the material passes over directly into the liquid form instead of traversing the continuous path. To expect the continuous process to take place, under these circumstances, is thus not unlike attempting to obtain a supersaturated solution in presence of a crystal of the dissolved salt. For a substance to follow freely the transition curve from gas to liquid, the absence of other kinds of matter, even of an envelope, is essential. Such a condensation is conceivable when the material condenses under its own mutual gravitation in a place apart from all other attracting matter.

We now turn to the corresponding case of a vapour becoming deposited on a surface of a solid through the mutual attraction between the particles of the solid and of the gas or, shortly, by " adsorption." The law of force—Laplace's law, $F = \sigma_1\sigma_2 f(r)$—is probably the same for this case as for where the forces are between the particles of the gas itself, only the " densities " σ_1 and σ_2 of the two attracting substances being different. Thus, we might expect a similar course of events to take place when under these forces condensation on a surface occurs, to that which takes place in the case of a gas following James Thomson's curve. If this were so, the character of the curve (fig. 2) experimentally found for the condensation or adsorption of water vapour on glass becomes explicable. When the pressure of the vapour in contact with a surface quite free from moisture gradually increases, the material at first condenses in a form which, for convenience, may be called the a form. The pressure goes up to a certain maximum value, after which it falls, owing to the material passing into the β or liquid form along a James Thomson curve. After this, on addition of sufficient material, the pressure can be increased up to saturation.

The question suggests itself: is there a case of adsorption of a vapour by a surface corresponding to the case of direct passage into the liquid from the gaseous state without going through the intermediate stage of the transition curve ? That is to say, if there were any of the material in the β or liquid state, would direct conversion into that state take place in a manner analogous to the usual direct path of condensation on a gas liquefying ?

The necessary condition—the presence of material in the β state—for this form of condensation, was found to be obtained by drying the glass wool with phosphorus pentoxide at ordinary temperatures for a time only just sufficient to reduce the pressure of the vapour to zero.

The results obtained with the material so dried are given in Table II, and are shown plotted in fig. 6. It will be seen that the curve, unlike the

previous curve, begins by being concave to the pressure co-ordinate and is thus similar in this respect to those obtained with wool and cotton.

Table II.

Weight per square centi- metre in arbitrary units.	Pressure in centimetres.	Weight per square centi- metre in arbitrary units.	Pressure in centimetres.
0·3	0·0075	7·5	0·909
0·5	0·010	8·3	0·989
1·3	0·020	9·5	1·060
2·0	0·216	10·7	1·165
3·0	0·480	12·2	1·243
3·8	0·583	12·9	1·249
5·0	0·698	13·8	1·271
6·0	0·688	14·8	1·330
6·8	0·837		

These pressures were reduced to a common temperature of 20° C. Observations were continued on to saturation, but are not given, as presenting nothing of interest.
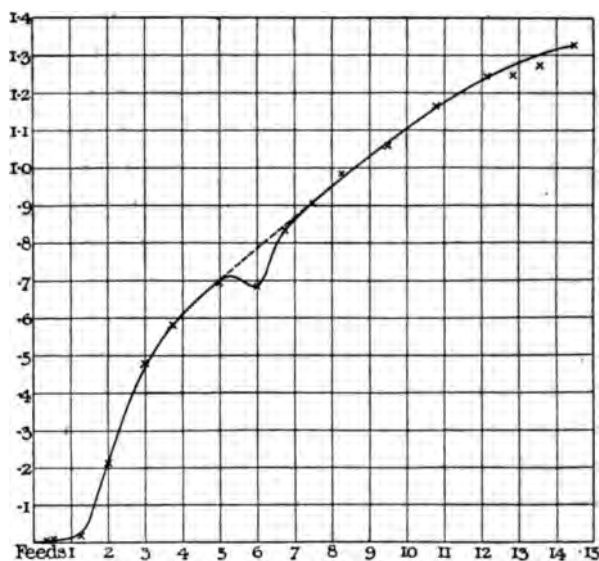
Fig. 6.

It is to be noticed that in this case, though the glass begins by being " wet " relatively to the glass in the previous case, yet a fresh quantity of water produces only a small increase in the pressure compared to what it produces when the glass is very dry.

The presence, then, of condensed vapour, or liquid, gives a nucleus, so to speak, for further condensations, or affords an example for condensation which

is absent in the case where more complete drying is effected. This would seem to require us to suppose that there are two modes in which the molecules of water in condensing can arrange themselves on the surface of the glass. Two other curves are given, fig. 7 and fig. 8, where the drying was at ordinary temperature but was continued for a longer period. In all these a slight indication of supersaturation will be noticed at about the same pressure as for the dry case. This may be due to a mixed effect brought about by a small quantity of the material being really dry, so that there is a small amount of absorption thus reducing the pressure.
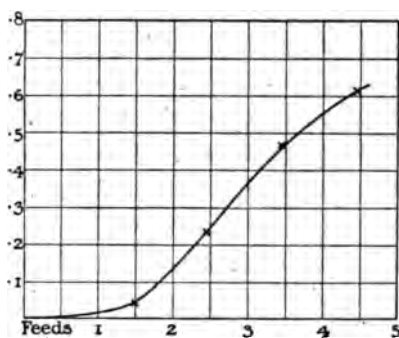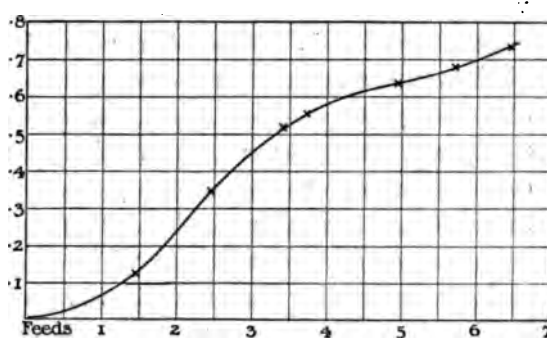
FIG. 7.   FIG. 8.

The phenomenon described throws light on a curious observation which, no doubt, all have noticed who have worked much with phosphorus-pentoxide drying tubes. The absorption of vapour is seen to be apparently confined to certain parts of the tube, and there the pentoxide may actually liquefy, while at other points it remains apparently dry. The explanation is that the wetter portion may absorb moisture without the pressure going up sensibly, while the relatively dry material can only absorb if the pressure goes up. In fact, a wet portion might be used to dry a drier portion.

A simple experiment to illustrate the effect can be easily made with two portions of phosphorus pentoxide in this way. Two small porcelain dishes are taken: one of these is dried by heating it red hot, while the other is left as it is with the usual condensed moisture from the atmosphere on it. Pentoxide is placed on both and they are then put under a bell-jar.

In a short time signs of condensation in the form of small liquid globules will appear round the edge of the pentoxide on the undried dish along the line of contact with it, also, perhaps, at a few points of dust over the surface of both portions of pentoxide. As the drying proceeds, it will be seen to be almost entirely effected by the portion in the undried dish, the other, except for a few globules on the surface, remaining unwet. In fact, if there is the proper quantity of moisture present in the bell-jar, the one will run liquid

while the other remains dry, except for the few specks mentioned. The action is, no doubt, due to the pentoxide in the first instance obtaining moisture from the porcelain surface which was left undried and thus forming a material to which moisture can be added, without the vapour pressure going rapidly up; whereas in the case of the dry salt, the pressure has first to reach a maximum or critical value before free absorption can take place.

. We may expect similar effects to take place in the case of other vapours or gases, that is to say, for two modes of condensation of a gas on solid surfaces to be possible, or, shortly, for the surface density not to be a single valued function of the pressure.

The variation in the pressure which is liable to take place in vacuum discharge tubes may, in part at least, be due to this phenomenon. Thus, with a given amount of gas in the tube, we would have the possibility of two stable modes of condensation, each with its own proper pressure. When the condensation is in the α state, the pressure is necessarily higher than when in the β state, as less is on the glass. The running of the tube, we may suppose, forces gas to take up the β state, which increases the proportion on the glass with a corresponding diminution in the pressure, while by means of external heating the α state may be restored with a rise in pressure.

The possibility for two layers of condensed vapour of different surface densities to be in equilibrium with the same vapour probably arises through molecular association in the β state and, in consequence, the tendency for molecules to escape into the space above the condensed layer being somehow lessened thereby; but it is not easy to say if this relative lessening in the β state as compared with the α state is to be attributed to an increased molecular force between the particles of the glass and those of the associated molecules in the β state or to the molecules in the α state being at a greater distance from those of the glass due to a looser molecular piling of the condensed surface layer.

Several important points suggest themselves in connection with the question of the two possible states in which vapour can condense on solid surfaces. It would be of interest, for instance, to be able to compare the conducting power for electricity of the surface layers on glass at the same vapour pressure, according as they are in the α or β state; also to ascertain what function of temperature the critical pressure is. Experiments for these purposes are now being undertaken.

The Mechanical Effects of Canal Rays.

By A. A. CAMPBELL SWINTON.

This investigation was undertaken in order to discover whether the so called canal rays (Canalstrahlen) discovered by Goldstein, which, at suitable pressures, visibly stream through the apertures in a perforated cathode, backward away from the anode, share with cathode rays the property discovered, as regards the latter, by Sir William Crookes many years ago, of producing a sufficient mechanical pressure to cause small and light mica mill-wheels to rotate. Several tubes were constructed and experimented with, and all showed that canal rays do cause mica mill-wheels to rotate quite rapidly.

Fig. 1 is the form of tube with which this was most conclusively demonstrated. A_1 is the anode, the lower end of which is tipped with a glass plate, so as to preclude the transmission of cathode rays vertically downwards in the event of this electrode acquiring at any moment a negative charge due to oscillations in the electric discharge.

A_2 is a supplemental anode, added since the paper was communicated, and referred to in the addendum.

C is the perforated cathode of aluminium, which is compound, consisting of C_1 of the cathode proper, perforated with six apertures. C_2 is a similar plate correspondingly perforated, and C_3 a third plate or shutter of aluminium also correspondingly perforated, loosely pivoted on a central pin between C_1 and C_2, and furnished with an armature D of soft iron, so that by means of a magnet it can be slightly rotated so as to open or close simultaneously all the six apertures A plan view of the shutter and armature is shown in Fig. 2.

FIG. 1.

It was found advisable to make C_1, C_3, and especially C_2 of thick plate, so as to avoid thermal effects.
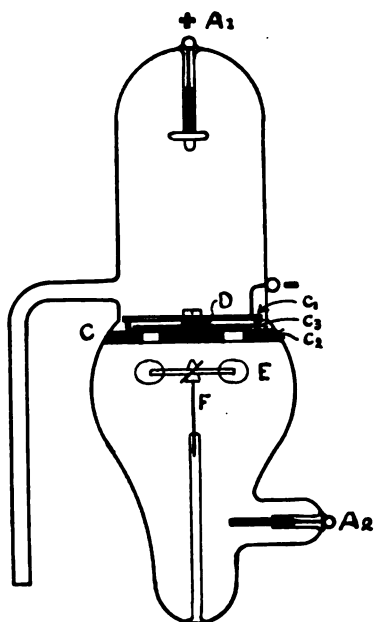
E is the mill-wheel of the screw propeller form, with mica vanes set at an oblique angle to the axis, mounted on a pivot F. The complete mill-wheel weighs about 0·19 gramme.
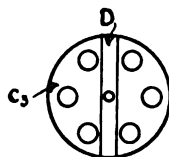

Fig. 2.

The experiments were conducted with the tube connected to a vacuum pump, so that the pressure could be regulated as desired. An induction coil was employed to produce the electrical discharge, a spark-gap being usually inserted in the circuit, with a view to obtaining currents only in one direction.

Rapid rotation of the mill-wheel, in the direction that would indicate that the canal rays consist of particles travelling away from the cathode, was easily obtained in all cases, the best results being got with medium vacua, when the canal rays were highly luminous.

That the effect was due to the action of the canal rays, was tested in several ways. Firstly, the shutter C_3 was rotated until all the apertures were closed. Under these conditions no rotation could be obtained, whereas when the apertures were open the mill-wheel was found to commence rotation the moment the current was turned on.

Again, the current was reversed and A made cathode in order to observe whether cathode rays from A might not be the cause of the rotation. This was found not to be the case. The upper part of the tube was also placed in a strong magnetic field, so as to deflect on to the walls of the tube any cathode rays reflected from the upper end of the tube, which, it was thought, might cause the rotation. As the motion was in no ways affected by the deflection of these reflected rays, it was obvious that the effect was not due to them.

It seems, therefore, clear that the rotation of the mill-wheel is caused by the canal rays impinging on the vanes of the former, though it appeared very probable that the effect was a secondary one, due to the rays making the vanes hotter on one side than on the other, with a consequent radiometer action, as is put forward by Professor J. J. Thomson,* as the true explanation of the rotation of mill-wheels under cathode ray bombardment.

This question of difference of temperatures on the two sides of the vanes of the mica mill-wheel was therefore investigated in a special tube, in which a small piece of mica furnished with two thermo-junctions of Constantan-copper, one on each side of the mica, arranged so as to oppose their E.M.F.'s, and connected to a mirror galvanometer, was placed behind the aperture in a perforated cathode, so as to be impinged upon by canal rays. Experiments

* 'Conduction of Electricity through Gases,' by J. J. Thomson, Second Edition, 1906, p. 629.

with this apparatus showed that the side of the mica vane struck by the canal rays was very much hotter than the other side, the difference in temperatures amounting to as much as 200° F. when the pressure was suitable.

It was also found that a maximum difference of temperature was obtained at those pressures which gave a maximum luminosity in the canal rays, which, as already mentioned, is the condition where the most rapid motion is imparted to the mill-wheel.

It thus appears that canal rays produce very similar mechanical effects as cathode rays, and in this connection the writer would draw attention to the experiment shown by Sir William Crookes, in 1891,* and the results obtained by the writer in 1898,† which show that mica mill-wheels, while rotating in one direction under the impact of cathode rays, revolve in the opposite direction if so placed in the tube so as to be just outside the cathode stream.

The canal rays are supposed to be streams of positively electrified particles which, travelling towards the cathode, pass through the apertures in the latter, and emerge on the other side. These mill-wheels would appear to demonstrate the motion of these particles, both when they are approaching the cathode, and after they have passed through the latter.

The writer is indebted to the assistance of Mr. J. C. M. Stanton and Mr. R. C. Pierce in carrying out the experiments.

[*Addendum, June* 6, 1907.—Since the above paper was communicated, further investigations have been conducted by the writer, all of which confirm the fact that canal rays do produce marked mechanical effects.

In the tube illustrated in fig. 3, A is the anode and C the aluminium cathode, with a single perforation which allows the canal rays to impinge on the mica vanes of the mill-wheel E, which is of the water-wheel type having vanes with their surfaces in radial planes parallel with the axis. This arrangement was found to be very effective, the mill-wheel rotating rapidly at suitable vacua in the direction indicated by the arrow, which is that which one would expect from canal ray bombardment.

An exactly similar tube, but fitted with a mill-wheel entirely constructed of aluminium, the vanes being of foil about 0·0127 mm. in thickness, gave exactly similar results, except that it appeared to require rather more power to make it work.

The tube illustrated in figs. 1 and 2 was also fitted with an additional

* "Electricity *in transitu* from Plenum to Vacuum," 'Journal of the Institution of Electrical Engineers,' vol. 20, No. 91, p. 25.
† 'Phil. Mag.,' October, 1898.

anode A₂. When this was employed in substitution for A₁, the mill-wheel was obviously subjected to the influence both of cathode rays proceeding from the cathode C, and also to the influence of canal rays streaming towards the cathode in the opposite direction.
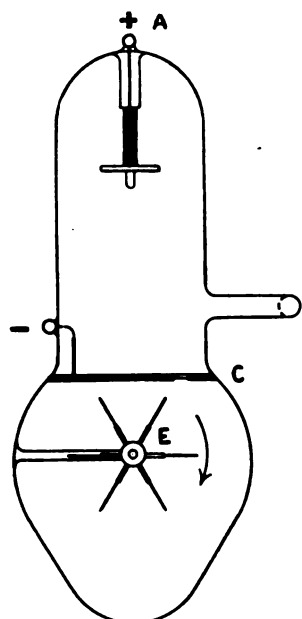

Fɪɢ. 3.

With this tube, with a mill-wheel with mica vanes, the cathode rays apparently had the more powerful effect, as both when the apertures in the cathode were open and also when they were closed the mill-wheel rotated invariably in the direction that corresponds with the motion being due to the cathode rays.

Another tube made according to figs. 1 and 2, but with the upper surfaces of the mica vanes of its mill-wheel coated with chloride of lithium, a salt which gives red fluorescence under canal ray bombardment, and blue fluorescence when the bombardment is by cathode rays, was also used. With this tube, when A₁ was anode, with the apertures in the cathode open, the wheel revolved and fluoresced red under the influence of the canal rays, while with A₂ as anode, the wheel turned in the same direction, but fluoresced blue under the bombardment of the cathode rays.

A further tube, constructed exactly as that illustrated in figs. 1 and 2, but with the mill-wheel and its vanes entirely constructed of aluminium foil about 0·0127 mm. in thickness and weighing altogether about 0·12 gramme, gave in one case different results. Using A₁ as anode, the rotation of the mill-wheel, when the apertures were open, was the same as that of the mill-wheel with mica vanes, being in the direction that would indicate that the effect was due to the canal rays; but when A₂ was made anode, the aluminium mill-wheel, instead of rotating as did the wheel with mica vanes in the direction that would correspond with the effect being due to cathode ray bombardment, was found to rotate with remarkable energy in the reverse direction, as would be caused by the canal rays proceeding towards the cathode. This was the case equally whether the apertures in the cathode were open or shut, the inference being that the force acting on the wheel due to positive particles approaching the cathode was in this case much greater than the force in the opposite direction due to the cathode ray corpuscles leaving the cathode.

In order to elucidate this divergence in the effect produced under as nearly as practicable similar circumstances upon mica mill-wheels on the one hand, and aluminium wheels on the other, further research seems necessary, but it would appear very probable that the heat insulating properties of mica, which would enable the two sides of a vane of this material to remain at widely different temperatures, and the high conductivity of aluminium for heat, which would not allow of such temperature differences, have an important bearing on this question.]

The Distribution of Blue and Violet Light in the Corona on August 30, 1905, as derived from Photographs taken at Kalaa-es-Senam, Tunisia.

By Dr. L. BECKER, Professor of Astronomy, University of Glasgow.

(Abstract.)

Nine photographs of the corona are available for discussion. They were all taken with the same instrument on the same plate (the two halves of a whole plate placed end to end) and developed in the same tray. A strong developer was used so as to produce as much contrast as possible. The plate had been exposed and moved onwards 1 or 2 inches after each exposure by an automatic device governed by a pendulum clock which closed and opened two electric circuits at specified intervals. The operator merely started the pendulum of the clock at the beginning of totality and the photographs were taken without further interference on his part. There are five exposures of 0·85 second, and one each of 9, 3, 89, 21, and 46 seconds duration. Owing to damage done in transit to the mechanism which propels the plate, the 3 seconds' exposure is partly superposed on the images belonging to those of 9 seconds and 89 seconds, with the result that only the sum of the exposures belonging to these two photographs is accurately known. This failure has somewhat complicated the reduction of the plates. During the first four exposures of 0·85 second the aperture of the lens was reduced respectively to 0·05, 0·09, 0·2, 0·4, of its area by screens, each of which had 13 equal openings distributed over the area of the lens. The effect due to diffraction produced by the screens is investigated in the

paper. The observations made on the photographs and utilised in this paper, consist in the selection of points on the several corona-images at which the photographic film shows the same degree of blackness, and in the measurement of their distance from the lunar disc. For instance, the first five photographs show the same degree of blackness at distances from the sun's limb of 0·063, 0·096, 0·139, 0·187, 0·263, respectively (unity $= 10^{-3}$ solar diameter). The measurements were actually made on positives which showed the corona as a transparent ring round the lunar disc, and not one but 24 points of an equal-blackness curve were measured. For the first five photographs the intensities of the corona at points where there is equal blackness are inversely as the areas of the exposed portions of the lens, while for the photographs taken at full aperture the intensity is a function of the duration of exposure, which function was determined from experiments. A complication arises from the fact that the intensity of the light diffusely reflected by the sky and various parts of the instrument is of the order of the intensity of the outlying coronal radiations. The observations thus give for a series of pairs of points whose distances from the moon's or sun's limb are known, the ratio of the intensities of light, and the problem is to represent the intensity as a function of the distance of the point from the sun's limb. The calculation was carried out only for the average distance of an equal-blackness (*i.e.*, intensity) curve, and the result is that the intensity of the corona decreases inversely as the fourth power of the average distance of the curve from a circle which is concentric with the sun's disc and whose diameter is about three-quarters of the solar diameter. The formula does not hold good in each of the 24 radial directions.

I have further attempted to refer the intensity to that of a certain region on the moon, utilising photographs of the moon which were taken at the Observatory after my return from the eclipse expedition. The object of the final sections of the paper is to show that such photographs as used here, if taken on ordinary plates and plates sensitised for red and yellow rays, would be well suited for settling the debated question whether or not the luminosity of the corona is actually caused by particles heated to luminescence by solar radiation.

Investigation of the Law of Burning of Modified Cordite.

By Major J. H. MANSELL, Royal Artillery.

(Abstract.)

Some years ago Vieille first propounded the law of combustion by parallel surfaces for smokeless propellants. This law has generally been accepted as correct.

Investigators have assumed that the relation is expressed by an equation of the form $S = aP^n$, where S is the skin burnt in a given time under the average pressure P, a and n being constants for the given explosive. The constants a and n have been obtained by a system of trial and error, testing the results obtained by calculation against the actual results obtained in a gun.

In the gun the space behind the projectile is treated as a closed vessel. As the projectile moves down the bore the size of this vessel increases, and the increase in a given time under a given pressure depends on what allowance is made for loss of effective pressure due to friction. The assumptions made as to frictional loss, combined with a hitherto unsuspected variation due to the form of the propellant, have led to wide differences in the values of a and n put forward.

In my experiments I used a closed vessel of constant capacity, the description and method of use of which are described in the complete paper.

The records obtained by this closed vessel enabled me to obtain, (1) the pressure density relation of M.D. cordite, and (2) the time rise of pressure at different densities of loading.

The first experiments were made with M.D. cordite in the cord form. From the time rise of pressure I was able to calculate what cordite had been burnt in a given time under the average pressure over that interval which was given me on the curve.

The relation found to exist is expressed by an equation of the form $S = aP + C$, where a varies with the initial temperature of the cordite. The constant C is thought to mean that below a pressure of about 0·1 ton on the square inch true explosion does not take place, and combustion by parallel surfaces over the whole charge is not going on. During this time the cordite is lit and burning slowly up to the point where true explosion begins.

Time-rises of pressure calculated from this formula show very close agreement with those actually obtained with cords.

Experiments were then made with the propellant in the tubular form. The time rise of pressure was found not to agree with that given by calculation, using the above formula. The rise at the beginning is much more rapid than would be expected from theory. A comparison of the actual and theoretical curves and observation of certain phenomena connected with the burning of tubes in the air led to the belief that there is excess pressure inside the tube even when burning explosively.

Calculations were therefore made to determine the amount of this excess internal pressure on the assumption that the fundamental law, as found for cords, must still be true.

The result of these calculations is the advancement of the theory that in the burning of tubes there is a two-phase condition: (1) when excess internal pressure exists; and (2) when it disappears. The amount of excess pressure depends on the size of the internal hole and length of the tube. Calculating on this principle, the theoretical time-rise shows agreement with the actual. By this theory one is also enabled to understand ballistic and other phenomena connected with the burning of tubes which are incapable of explanation on the assumption of a relation of the form $S = aP^n$.

Experiments were then made with the propellant in the double tubular form, and the influence of excess internal pressure is shown to be more marked than with the tubular.

It is this form-influence on the time-rise which in part accounts for the great variation in formulas put forward by various investigators.

The results of this investigation have been applied to the practical case of the gun. Having adopted certain frictional laws, the application with cords, with which we have most experience, has been found to hold over a wide range of varying conditions of loading and calibre.

On the Dynamical Theory of Gratings.

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In the usual theory of gratings, upon the lines laid down by Fresnel, the various parts of the primary wave-front after undergoing influences, whether affecting the phase or the amplitude, are conceived to pursue their course as if they still formed the fronts of waves of large area. This supposition, justifiable as an approximation when the grating interval is large, tends to fail altogether when the interval is reduced so as to be comparable with the wave-length. A simple example will best explain the nature of the failure. Consider a grating of perfectly reflecting material whose alternate parts are flat and parallel and equally wide, but so disposed as to form a groove of depth equal to a quarter wave-length, and upon this let light be incident perpendicularly. Upon Fresnel's principles the central regularly reflected
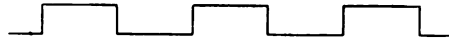
FIG. 1.

image must vanish, being constituted by the combination of equal and opposite vibrations. If the grating interval be large enough, this conclusion is approximately correct and could be verified by experiment. But now suppose that the grating interval is reduced until it is less than the wave-length of the light. The conclusion is now entirely wide of the mark. Under the circumstances supposed there are no lateral spectra and the *whole* of the incident energy is necessarily thrown into the regular reflection, which is accordingly total instead of evanescent. A closer consideration shows that the recesses in this case act as resonators in a manner not covered by Fresnel's investigations, and illustrates the need of a theory more strictly dynamical.

The present investigation, of which the interest is mainly optical, may be regarded as an extension of that given in 'Theory of Sound,'* where plane waves were supposed to be incident perpendicularly upon a regularly corrugated surface, whose form was limited by a certain condition of symmetry. Moreover, attention was there principally fixed upon the case where the wave-length of the corrugations was long in comparison with that

* Second edition, § 272u, 1896.

of the waves themselves, so that in the optical application there would be a large number of spectra. It is proposed now to dispense with these restrictions. On the other hand, it will be supposed that the *depth* of the corrugations is small in comparison with the length (λ) of the waves.

The equation of the reflecting surface may be taken to be $z = \zeta$, where ζ is a periodic function of x, whose mean value is zero, and which is independent of y. By Fourier's theorem we may write

$$\zeta = c_1 \cos px + c_2 \cos 2px + s_2 \sin 2px + \dots + c_n \cos npx + s_n \sin npx + \dots$$

$$= \tfrac{1}{2}c_1 (e^{ipx} + e^{-ipx}) + \tfrac{1}{2}(c_n - is_n) e^{inpx} + \tfrac{1}{2}(c_n + is_n) e^{-inpx} + \dots, \tag{1}$$

the wave-length (ϵ) of the corrugation being $2\pi/p$. Formerly the s terms were omitted and attention was concentrated upon the case where c_1 was alone sensible. The omission of the s terms makes the grating symmetrical, so that at perpendicular incidence the spectra on the two sides are similar. It is known that this condition is often, and indeed advantageously, departed from in practice.
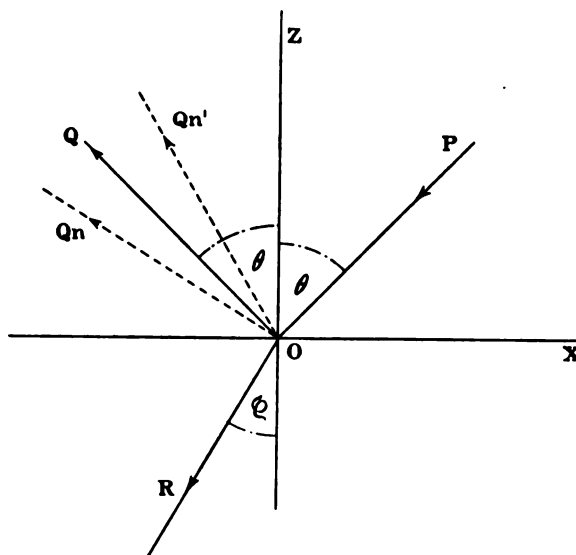
Fig. 2.

The vibrations incident at obliquity θ, POZ, fig. 2, are represented by

$$\psi = e^{ik(Vt + x\cos\theta + z\sin\theta)}, \tag{2}$$

where $k = 2\pi/\lambda$, and V is the velocity of propagation in the upper medium. Here ψ satisfies in all cases the same general differential equation, but its significance must depend upon the character of the waves. In the acoustical application, to which for the present we may confine our attention, ψ is the

velocity-potential. In optics it is convenient to change the precise interpretation according to circumstances, as we shall see later.

The waves regularly reflected along OQ are represented by

$$\psi = A_0 \, e^{ik(Vt - s \cos \theta + x \sin \theta)}, \tag{3}$$

in which A_0 is a (possibly complex) coefficient to be determined. In all the expressions with which we have to deal the time occurs only in the factor e^{ikVt}, running through. For brevity this factor may be omitted.

In like manner the waves regularly refracted along OR into the lower medium have the expression

$$\psi_1 = B_0 \, e^{ik_1(s \cos \phi + z \sin \phi)}, \tag{4}$$

ϕ being the angle of refraction; and, by the law of refraction,

$$k_1 : k = V : V_1 = \sin \theta : \sin \phi. \tag{5}$$

In addition to the incident and regularly reflected and refracted waves, we have to consider those corresponding to the various *spectra*. For the reflected spectra of the nth order we have

$$\psi = A_n \, e^{ik(-s \cos \theta_n + z \sin \theta_n)} + A'_n \, e^{ik(-s \cos \theta'_n + z \sin \theta'_n)}, \tag{5'}$$

where, by the elementary theory of these spectra,

$$\epsilon \sin \theta_n - \epsilon \sin \theta = \pm n\lambda, \quad \text{or} \quad \sin \theta_n - \sin \theta = \pm n\lambda/\epsilon = \pm np/k. \tag{6}$$

We shall choose the upper sign for θ_n and the lower for θ'_n. In virtue of (6) the complete expression for ψ in the upper medium takes the form

$$\psi \cdot e^{-ikx \sin \theta} = e^{ikx \cos \theta} + A_0 \, e^{-ikx \cos \theta} + \dots$$
$$+ A_n \, e^{inpx} \, e^{-ikx \cos \theta_n} + A'_n \, e^{-inpx} \, e^{-ikx \cos \theta'_n} + \dots, \tag{7}$$

where n has in succession the values 1, 2, 3, etc.

Similarly, in the lower medium the spectra of the nth order are represented by

$$\psi_1 = B_n \, e^{ik_1(s \cos \phi_n + x \sin \phi_n)} + B'_n \, e^{ik_1(s \cos \phi'_n + x \sin \phi'_n)}, \tag{8}$$

where
$$\sin \phi_n - \sin \phi = \pm np/k_1. \tag{9}$$

Accordingly, for the complete expression of ψ_1, we have with use of (5),

$$\psi_1 \cdot e^{-ikx \sin \theta} = B_0 \, e^{ik_1 s \cos \phi} + \dots + B_n \, e^{inpx} \, e^{ik_1 s \cos \phi_n} + B'_n \, e^{-inpx} \, e^{ik_1 s \cos \phi'_n}. \tag{10}$$

We must now introduce boundary conditions to be satisfied at the transition between the two media when $z = \zeta$. It may be convenient to commence with a very simple case determined by the condition that $\psi = 0$. The whole of the incident energy is then thrown back, and is distributed between the regularly reflected waves and the various reflected spectra.

We proceed by approximation depending on the smallness of ζ. Expanding the exponentials on the right side of (7), we get

$$(1+A_0)(1-\tfrac{1}{2}k^2\zeta^2\cos^2\theta+\dots)+(1-A_0)(ik\zeta\cos\theta+\dots)$$

$$+A_n e^{inpx}(1-ik\zeta\cos\theta_n+\dots)+A'_n e^{-inpx}(1-ik\zeta\cos\theta'_n+\dots)=0. \quad (11)$$

In this equation the value of ζ is to be substituted from (1), and then in accordance with Fourier's theorem the coefficients of the various exponential terms, such as e^{inpx}, e^{-inpx}, are to be separately equated to zero. As the first approximation, we get from the constant term (independent of x)

$$1+A_0=0, \quad (12)$$

and from the terms in e^{inpx}, e^{-inpx},

$$A_n = -ik\cos\theta\,(c_n-is_n), \quad A'_n = -ik\cos\theta\,(c_n+is_n). \quad (13)$$

Thus, as was to be expected, A_n, A'_n are of the first order in ζ, and if we stop at the second order inclusive, (11) may be written

$$1+A_0+2ik\zeta\cos\theta+A_n e^{inpx}(1-ik\zeta\cos\theta_n)+A'_n e^{-inpx}(1-ik\zeta\cos\theta'_n)=0. \quad (14)$$

For the second approximation to A_0 we get

$$1+A_0-\tfrac{1}{2}k^2\cos\theta\,\Sigma\,(c_n^2+s_n^2)(\cos\theta_n+\cos\theta'_n)=0. \quad (15)$$

By means of (13) and (15) we may verify the principle that the energies of the incident, and of all the reflected vibrations taken together, are equal. The energy corresponding to unit of wave-front of the incident waves may be supposed to be unity, and for the other waves $\mathrm{mod}^2 A_0$, $\mathrm{mod}^2 A_1$, $\mathrm{mod}^2 A'_1$, etc. But what we have to consider are not equal areas of wave-front, but areas corresponding to the same extent of reflecting surface, *i.e.*, areas of wave-front proportional to $\cos\theta$, $\cos\theta_1$, $\cos\theta'_1$, etc. Hence,

$$\cos\theta\,.\,\mathrm{mod}^2 A_0+\Sigma\,\cos\theta_n\,.\,\mathrm{mod}^2 A_n+\Sigma\,\cos\theta'_n\,.\,\mathrm{mod}^2 A'_n = \cos\theta, \quad (16)$$

with which the special approximate values already given are in harmony. In the formation of (16) only real values of $\cos\theta_n$, $\cos\theta'_n$ are to be included. If $p>k$, no real values exist, *i.e.*, there are no lateral spectra. The regular reflection is then total, and this without limitation upon the magnitude of the c's. The question is further considered in 'Theory of Sound,' § 272 *a*.

In pursuing a second approximation for the coefficients of the lateral spectra, we will suppose for the sake of brevity that the *s* terms in (1) are omitted. From the term involving e^{inpx} in (14), we get with use of (13),

$$A_n = -ik \cos \theta \, c_n + \tfrac{1}{2}k^2 \cos \theta \cos \theta'_n \, c_n \, c_{2n}$$

$$+ \tfrac{1}{2}k^2 \cos \theta \, \{(c_1 \cos \theta_{n-1} + c_{2n-1} \cos \theta'_{n-1}) \, c_{n-1}$$

$$+ (c_2 \cos \theta_{n-2} + c_{2n-2} \cos \theta'_{n-2}) \, c_{n-2} + \dots$$

$$+ (c_1 \cos \theta_{n+1} + c_{2n+1} \cos \theta'_{n+1}) \, c_{n+1}$$

$$+ (c_2 \cos \theta_{n+2} + c_{2n+2} \cos \theta'_{n+2}) \, c_{n+2} + \dots\}, \tag{17}$$

in which the first (descending) series is to terminate when the suffix in $\cos \theta_{n-r}$ is equal to unity.

The value of A'_n may be derived from (17) by interchange of θ' and θ in $\cos \theta_{n-r}$, $\cos \theta'_{n-r}$, $\cos \theta_{n+r}$, $\cos \theta'_{n+r}$, $\cos \theta$ remaining unchanged. As a particular case of (17), we have, for the spectra of the first order,

$$A_1 = -ikc_1 \cos \theta + \tfrac{1}{2}k^2 c_1 c_2 \cos \theta \cos \theta'_1$$

$$+ \tfrac{1}{2}k^2 \cos \theta \, \{c_2 (c_1 \cos \theta_2 + c_3 \cos \theta'_2)$$

$$+ c_3 (c_2 \cos \theta_3 + c_4 \cos \theta'_3) + \dots\}. \tag{18}$$

$$A'_1 = -ikc_1 \cos \theta + \tfrac{1}{2}k^2 c_1 c_2 \cos \theta \cos \theta_1$$

$$+ \tfrac{1}{2}k^2 \cos \theta \, \{c_2 (c_1 \cos \theta'_2 + c_3 \cos \theta_2)$$

$$+ c_3 (c_2 \cos \theta'_3 + c_4 \cos \theta_3) + \dots\}, \tag{19}$$

the descending series in (17) disappearing altogether.

If the incidence is normal, $\cos \theta = 1$, $\cos \theta'_n = \cos \theta_n$, and thus A_n, A'_n become identical and assume specially simple forms. Referring to (7), we see that in this case

$$\psi = e^{ikz} + A_0 e^{-ikz} + 2A_1 e^{-ikz \cos \theta_1} \cos px + \dots + 2A_n e^{-ikz \cos \theta_n} \cos npx + \dots, \tag{20}$$

in which, to the second order,

$$A_0 = -1 + k^2 \Sigma c_n^2 \cos \theta_n. \tag{21}$$

$$A_n = -ikc_n + \tfrac{1}{2}k^2 \cos \theta_n \cdot c_n c_{2n}$$

$$+ \tfrac{1}{2}k^2 \, \{(c_1 + c_{2n-1}) c_{n-1} \cos \theta_{n-1} + (c_2 + c_{2n-2}) c_{n-2} \cos \theta_{n-2} + \dots$$

$$+ (c_1 + c_{2n+1}) c_{n+1} \cos \theta_{n+1} + (c_2 + c_{2n+2}) c_{n+2} \cos \theta_{n+2} + \dots\}. \tag{22}$$

If we suppose that in (1) only c_1 and c_2 are sensible, we have

$$A_0 = -1 + k^2 c_1^2 \cos \theta_1 + k^2 c_2^2 \cos \theta_2, \tag{23}$$

$$A_1 = -ikc_1 + \tfrac{1}{2}k^2 c_1 c_2 (\cos \theta_1 + \cos \theta_2), \tag{24}$$

$$A_2 = -ikc_2 + \tfrac{1}{2}k^2 c_1^2 \cos \theta_1, \tag{25}$$

$$A_3 = \tfrac{1}{2}k^2 c_1 c_2 (\cos \theta_1 + \cos \theta_2), \tag{26}$$

while A_4, A_5, etc., vanish to the second order of small quantities inclusive.

There is no especial difficulty in carrying the approximations further. As

an example, we may suppose that c_1 is alone sensible in (1), so that we may write

$$\zeta = c \cos px, \qquad (27)$$

and also that the incidence is perpendicular. For brevity we will denote $k \cos \theta_n$ or $k \cos \theta'_n$ by μ_n. The boundary condition ($\psi = 0$) becomes by (7) in this case,

$$e^{ik\zeta} - e^{-ik\zeta} + (A_0 + 1) e^{-ik\zeta} + 2A_1 e^{-i\mu_1\zeta} \cos px$$
$$+ \ldots\ldots + 2A_n e^{-i\mu_n\zeta} \cos npx + \ldots\ldots = 0, \qquad (28)$$

in which

$$e^{ik\zeta} - e^{-ik\zeta} = 4i \{J_1(kc) \cos px - J_3(kc) \cos 3px + J_5(kc) \cos 5px - \ldots\}, \qquad (29)$$
$$e^{-ik\zeta} = J_0(kc) - 2J_2(kc) \cos 2px + \ldots$$
$$- i \{2J_1(kc) \cos px - 2J_3(kc) \cos 3px + \ldots\}, \qquad (30)$$

with similar expressions for $e^{-i\mu_1\zeta}$, $e^{-i\mu_n\zeta}$, etc. By Fourier's theorem the terms independent of x, in $\cos px$, $\cos 2px$, etc., must vanish separately. The first gives

$$(A_0 + 1) J_0(kc) - 2iA_1 J_1(\mu_1 c) - 2A_2 J_2(\mu_2 c) + 2iA_3 J_3(\mu_3 c) + 2A_4 J_4(\mu_4 c) + \ldots = 0. \qquad (31)$$

The term in $\cos px$ gives

$$2i J_1(kc) - i(A_0 + 1) J_1(kc) + A_1 \{J_0(\mu_1 c) - J_2(\mu_1 c)\}$$
$$- iA_2 \{J_1(\mu_2 c) - J_3(\mu_2 c)\} - A_3\{J_2(\mu_3 c) - J_4(\mu_3 c)\} + \ldots = 0. \qquad (32)$$

The term in $\cos 2px$ gives

$$-(A_0 + 1) J_2(kc) - iA_1 \{J_1(\mu_1 c) - J_3(\mu_1 c)\}$$
$$+ A_2 \{J_0(\mu_2 c) + J_4(\mu_2 c)\} + \ldots\ldots = 0. \qquad (33)$$

The term in $\cos 3px$ gives

$$-2i J_3(kc) + i(A_0 + 1) J_3(kc)$$
$$- A_1 \{J_2(\mu_1 c) - J_4(\mu_2 c)\} - iA_2 \{J_1(\mu_2 c) + J_5(\mu_2 c)\}$$
$$+ A_3 \{J_0(\mu_3 c) - J_6(\mu_3 c)\} + \ldots\ldots = 0. \qquad (34)$$

We see from these that $A_0 + 1$ is of the second order in kc, that A_1 is of the first order, A_2 of the second order, A_3 of the third order, and so on. Expanding the Bessel's functions, we find, to the second order inclusive, as in (23), (24), (25), (26),

$$\left. \begin{array}{ll} A_0 = -1 + k\mu_1 c^2, & A_1 = -ikc, \\ A_2 = \tfrac{1}{2}k\mu_1 c^2, & A_3 = 0. \end{array} \right\}, \qquad (35)$$

A_4, etc., vanishing. To the third order inclusive (34) now gives

$$A_3 = \tfrac{1}{24} ikc^3 (k^2 - 3\mu_1^2 + 6\mu_1\mu_2). \qquad (36)$$

From (33) to the same order we have still for A_2,

$$A_2 = \tfrac{1}{2}k\mu_1 c^2, \qquad (37)$$

and from (32)

$$A_1 = -ikc + \tfrac{1}{8} ikc^3 (k^2 + 4k\mu_1 + 2\mu_1\mu_2 - 3\mu_1^2). \qquad (38)$$

These are complete to the third order of kc inclusive. To this order A_4, A_5, etc., vanish.

So far as the third order of kc inclusive, A_0 remains as in (35); but it is worth while here to retain the terms of the fourth order. We find from (31)—

$$A_0 = -1 + k\mu_1 c^2 + \tfrac{1}{8}kc^4 (k^3\mu_1 - 4k\mu_1^2 + 2\mu_1^3 - 2\mu_1^2\mu_2 + \mu_1\mu_2^2). \qquad (39)$$

It is to be noted that k, μ_1, μ_2 are not independent. By (6), with $\theta = 0$,

$$\mu_n^2 = k^2 \cos^2 \theta_n = k^2 - n^2 p^2, \qquad (40)$$

so that

$$\mu_1^2 = k^2 - p^2, \qquad \mu_2^2 = k^2 - 4p^2,$$

and

$$3k^2 - 4\mu_1^2 + \mu_2^2 = 0. \qquad (41)$$

By use of (41) it may be verified to the fourth order that when μ_1, μ_2 are real, so that the spectra of the second order are actually formed,

$$\mathrm{mod}^2 A_0 + \frac{2\mu_1}{k}\,\mathrm{mod}^2 A_1 + \frac{2\mu_2}{k}\,\mathrm{mod}^2 A_2 = 1, \qquad (42)$$

expressing the conservation of vibratory energy.

When μ_1 is real, but not μ_2, we may write $\mu_2 = -i\nu_2$, where ν_2 is positive. In this case

$$A_0 = -1 + k\mu_1 c^2 + \tfrac{1}{8}kc^4 (k^3\mu_1 - 4k\mu_1^2 + 2\mu_1^3 - \mu_1\nu_2^2) + \tfrac{1}{4}ikc^4\mu_1^2\nu_2,$$

$$A_1 = -ikc + \tfrac{1}{8}ikc^3 (k^2 + 4k\mu_1 - 3\mu_1^2) + \tfrac{1}{4}kc^3\mu_1\nu_2 ;$$

and in virtue of (41) to the fourth order,

$$\mathrm{mod}^2 A_0 + \frac{2\mu_1}{k}\,\mathrm{mod}^2 A_1 = 1. \qquad (43)$$

Again, if μ_1, μ_2 are both imaginary, equal, say, to $-i\nu_1$, $-i\nu_2$, we have from (39) with separation of real and imaginary parts,

$$A_0 = -1 + \tfrac{1}{2}k^2\nu_1^2 c^4 - i (k\nu_1 c^2 + \text{terms in } c^4),$$

so that, to the fourth order,

$$\mathrm{mod}^2 A_0 = 1, \qquad (44)$$

expressing that the regular reflection is now total.

In the acoustical interpretation for a gaseous medium ψ represents the velocity-potential, and the boundary condition ($\psi = 0$) is that of constant pressure. In the electrical and optical interpretation the waves are incident from air, or other dielectric medium, upon a perfectly conducting and, therefore, perfectly reflecting corrugated substance. Here ψ represents the electromotive intensity Q parallel to y, that is parallel to the lines of the grating, the boundary condition being the evanescence of Q.

We now pass on to the boundary condition next in order of simplicity, which ordains that $d\psi/dn = 0$, where dn is drawn normally at the surface of separation. Since the surfaces $z - \zeta = 0$, $\psi = $ constant, are to be perpendicular, the condition expressed in rectangular co-ordinates is

$$\frac{d\psi}{dz} - \frac{d\psi}{dx} \frac{d\zeta}{dx} = 0, \tag{45}$$

ψ being given by (7) and ζ by (1).

For the purposes of the first approximation, we require in $d\psi/dx$ only the part independent of the c's and s's, since $d\zeta/dx$ is already of the first order. Thus at the surface

$$\frac{d\psi}{dx} = ik \sin \theta \, e^{ikx \sin \theta} (1 + A_0).$$

Also, correct to the first order,

$$\frac{d\psi}{dz} = ik \, e^{ikx \sin \theta} [\cos \theta \{1 - A_0 + (1 + A_0) \, ik\zeta \cos \theta\}$$

$$-\ldots\ldots - \cos \theta_n A_n \, e^{inpx} - \cos \theta'_n A'_n \, e^{-inpx}].$$

Thus (45) gives

$$\cos \theta (1 - A_0) + \cos^2 \theta (1 + A_0) \, ik\zeta - \cos \theta_n A_n \, e^{inpx}$$

$$-\cos \theta'_n A'_n \, e^{-inpx} - \ldots\ldots - \sin \theta (1 + A_0) \frac{d\zeta}{dx} = 0. \tag{46}$$

From the term independent of x we see that, as was to be expected,

$$A_0 = 1. \tag{47}$$

Also $$A_n \cos \theta_n = i (c_n - is_n) \{k \cos^2 \theta - np \sin \theta\}, \tag{48}$$

$$A'_n \cos \theta'_n = i (c_n + is_n) \{k \cos^2 \theta + np \sin \theta\}. \tag{49}$$

When $n = 1$ in (48), (49), we may put $s_1 = 0$. These equations constitute the complete solution to a first approximation.

For the second approximation we must retain the terms of the first order in $d\psi/dx$. Thus from (5), (7)

$$e^{-ikx \sin \theta} \frac{d\psi}{dx} = ik \, [\sin \theta \{1 + A_0 + (1 - A_0) \, ik \cos \theta\}$$

$$+ \sin \theta_n A_n \, e^{inpx} + \sin \theta'_n A'_n \, e^{-inpx}]$$

$$= ik \{2 \sin \theta + \sin \theta_n A_n \, e^{inpx} + \sin \theta'_n A'_n \, e^{-inpx}\}, \tag{50}$$

since to the first order inclusive $A_0 = 1$. Also

$$e^{-ikx \sin \theta} \frac{d\psi}{dz} = ik \cos \theta \{1 - A_0 + 2ik\zeta \cos \theta\}$$

$$-ik \cos \theta_n A_n \, e^{inpx} (1 - ik\zeta \cos \theta_n) - ik \cos \theta'_n A'_n \, e^{-inpx} (1 - ik\zeta \cos \theta'_n). \tag{51}$$

Thus by (45) the boundary condition is

$$\cos\theta\,(1-A_0)+2ik\zeta\cos^2\theta-2\sin\theta\frac{d\zeta}{dx}$$

$$-A_n\,e^{inpx}\left\{\cos\theta_n-ik\cos^2\theta_n\,\zeta+\sin\theta_n\frac{d\zeta}{dx}\right\}$$

$$-A'_n\,e^{-inpx}\left\{\cos\theta'_n-ik\cos^2\theta'_n\,\zeta+\sin\theta'_n\frac{d\zeta}{dx}\right\}=0.\qquad(52)$$

In the small terms we may substitute for A_n, A'_n their approximate values from (48), (49).

In (52) the coefficients of the various terms in e^{inpx}, e^{-inpx} must vanish separately. In pursuing the approximation we will write for brevity

$$\zeta=\zeta_1\,e^{ipx}+\zeta_{-1}\,e^{-ipx}+\ldots+\zeta_n\,e^{inpx}+\zeta_{-n}\,e^{-inpx},\qquad(53)$$

where, $$\zeta_1=\zeta_{-1}=\tfrac{1}{2}c_1,$$

and $$\zeta_n=\tfrac{1}{2}\,(c_n-is_n),\qquad \zeta_{-n}=\tfrac{1}{2}\,(c_n+is_n).\qquad(54)$$

The term independent of x gives A_0 to the second approximation. Thus

$$\cos\theta\,(1-A_0)+iA_n\,(k\cos^2\theta_n+np\sin\theta_n)\,\zeta_{-n}$$

$$+iA'_n\,(k\cos^2\theta'_n-np\sin\theta'_n)\,\zeta_n=0.\qquad(55)$$

In (55), as follows from (6),

$$k\cos^2\theta_n+np\sin\theta_n=k\cos^2\theta-np\sin\theta,$$

and $$k\cos^2\theta'_n-np\sin\theta'_n=k\cos^2\theta+np\sin\theta.$$

Hence with introduction of the values of A_n, A'_n from (48), (49),

$$\cos\theta\,(1-A_0)=\ldots\ldots+\frac{c_n^2+s_n^2}{2\cos\theta_n}(k\cos^2\theta-np\sin\theta)^2$$

$$+\frac{c_n^2+s_n^2}{2\cos\theta'_n}(k\cos^2\theta+np\sin\theta)^2+\ldots\ldots,\qquad(56)$$

as might also be inferred from (48), (49) alone, with the aid of the energy equation—

$$\cos\theta=\cos\theta\,\mathrm{mod}^2A_0+\ldots+\cos\theta_n\,\mathrm{mod}^2A_n+\cos\theta'_n\,\mathrm{mod}^2A'_n.\qquad(57)$$

From the term in e^{inpx} in (52) we get

$$\cos\theta_nA_n=2i\,(k\cos^2\theta-np\sin\theta)\,\zeta_n$$

$$+iA'_n\,(k\cos^2\theta'_n-2np\sin\theta'_n)\,\zeta_{2n}+\ldots\ldots$$

$$+i\,A_{n-r}\,(k\cos^2\theta_{n-r}-rp\sin\theta_{n-r})\,\zeta_r$$

$$+i\,A_{n+r}\,(k\cos^2\theta_{n+r}+rp\sin\theta_{n+r})\,\zeta_{-r}$$

$$+i\,A'_{n-r}\,(k\cos^2\theta'_{n-r}-(2n-r)p\sin\theta'_{n-r})\,\zeta_{2n-r}$$

$$+iA'_{n+r}\,(k\cos^2\theta'_{n+r}-(2n+r)p\sin\theta'_{n+r})\,\zeta_{2n+r}.\qquad(58)$$

In (58) r is to assume the values 1, 2, 3, etc., the descending series terminating when $n - r = 1$.

The corresponding equation for A'_n may be derived from (58) by changing the sign of n, with the understanding that

$$A_{-m} = A'_m, \qquad A'_{-m} = A_m; \qquad \theta_{-m} = \theta'_m, \qquad \theta'_{-m} = \theta_m. \qquad (59)$$

If the incidence be perpendicular, so that $\theta'_m = -\theta_m$, and if $\zeta_{-m} = \zeta_m$, which requires that $s_m = 0$, the values of A'_n and A_n become identical.

If $n = 1$, the descending series in (58) make no contribution. We have

$$\cos\theta_1 A_1 = 2i\,(k\cos^2\theta - p\sin\theta)\,\zeta_1 + iA'_1\,(k\cos^2\theta'_1 - 2p\sin\theta'_1)\,\zeta_2$$
$$+ iA_2\,(k\cos^2\theta_2 + p\sin\theta_2)\,\zeta_{-1} + iA_3\,(k\cos^2\theta_3 + 2p\sin\theta_3)\,\zeta_{-2} + \dots$$
$$+ iA'_2\,(k\cos^2\theta'_2 - 3p\sin\theta'_2)\,\zeta_3 + iA'_3\,(k\cos^2\theta'_3 - 4p\sin\theta'_3)\,\zeta_4 + \dots \qquad (60)$$

We will now introduce the simplifying suppositions that $\theta = 0$, $s_m = 0$, making $A'_n = A_n$, and also that only c_1 and c_2 are sensible, so that $\zeta_3 = \zeta_4 = \dots\dots = 0$. We will also, as before, denote $k\cos\theta_n$ or $k\cos\theta'_n$ by μ_n. Accordingly (60) gives, with use of (6), (48), (49),

$$A_1 = \frac{ik^3 c_1}{\mu_1} - \frac{k^3 c_1 c_2}{2\mu_1^2}(\mu_1^2 + 2p^2) - \frac{k^3 c_1 c_2}{2\mu_1\mu_2}(\mu_2^2 + 2p^2). \qquad (61)$$

In like manner, we get from (58)

$$A_2 = \frac{ik^3 c_2}{\mu_2} - \frac{k^3 c_1^2}{2\mu_1\mu_2}(\mu_1^2 - p^2), \qquad (62)$$

$$A_3 = -\frac{k^3 c_1 c_2(\mu_1 + \mu_2)}{2\mu_3}\left\{1 - \frac{2p^2}{\mu_1\mu_2}\right\}, \qquad (63)$$

$$A_4 = -\frac{k^3 c_2^2}{2\mu_2\mu_4}(\mu_2^2 - 4p^2), \qquad (64)$$

after which A_5, A_6, etc., vanish to this order of approximation. In any of these equations we may replace μ_n^2 by its value from (6), that is $k^2 - n^2 p^2$.

The boundary condition of this case, i.e., $d\psi/dn = 0$, is realised acoustically when aerial waves are incident upon an immovable corrugated surface. In the interpretation for electrical and luminous waves, ψ represents the magnetic induction (b) paralled to y, so that the electric vector is perpendicular to the lines of the grating, the boundary condition at the surface of a perfect reflector being $db/dn = 0$.

We have thus obtained the solutions for the two principal cases of the incidence of polarised light upon a perfect corrugated reflector. In comparing

the results for the first order of approximation as given in (13) for the first case and in (48), (49) for the second, we are at once struck with the fact that in the second case, though not in the first, the intensity of a spectrum may become infinite through the evanescence of $\cos \theta_n$ or $\cos \theta'_n$, which occurs when the spectrum is just disappearing from the field of view. But the effect is not limited to the particular spectrum which is on the point of disappearing. Thus in (61) A_1, giving the spectrum of the *first* order, becomes infinite as the spectrum of the *second* order disappears ($\mu_2 = 0$). Regarded from a mathematical point of view, the method of approximation breaks down. The problem has no definite solution, so long as we maintain the suppositions of perfect reflection, of an infinite train of simple waves, and of a grating infinitely extended in the direction perpendicular to its ruling. But under the conditions of experiment, we may at least infer the probability of abnormalities in the brightness of any spectrum at the moment when one of higher order is just disappearing, abnormalities limited, however, to the case where the electric displacement is perpendicular to the ruling.* It may be remarked that when the incident light is unpolarised, the spectrum about to disappear is polarised in a plane parallel to the ruling.

In both the cases of boundary conditions hitherto treated, the circumstances are especially simple in that the aggregate reflection is perfect, the whole of the incident energy being returned into the upper medium. We now pass on to more complicated conditions, which we may interpret as those of two gaseous media of densities σ and σ_1. Equality of pressures at the interface requires that

$$\sigma \psi = \sigma_1 \psi_1, \tag{65}$$

and we have also to satisfy the continuity of normal velocity expressed by

$$d\psi/dn = d\psi_1/dn, \tag{66}$$

or, as in (45),

$$\frac{d(\psi - \psi_1)}{dz} - \frac{d(\psi - \psi_1)}{dx} \frac{d\zeta}{dx} = 0, \tag{67}$$

ψ and ψ_1 being given by (7), (10). We must content ourselves with a solution to the first approximation, at least for general incidence.

From (65),

$$\frac{\sigma}{\sigma_1} \{1 + A_0 + (1 - A_0) ik\zeta \cos \theta + A_n e^{inpx} + A'_n e^{-inpx}\}$$

$$= B_0 (1 + ik_1\zeta \cos \phi) + B_n e^{inpx} + B'_n e^{-inpx}. \tag{68}$$

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* See a "Note on the Remarkable Case of Diffraction Spectra described by Professor Wood," recently communicated to the 'Philosophical Magazine,' vol. 14, p. 60, 1907.

Distinguishing the various components in ζ as in (53), we find

$$\frac{\sigma}{\sigma_1}(1 + A_0) = B_0, \tag{69}$$

$$\frac{\sigma}{\sigma_1} A_n - B_n = i\zeta_n \left\{ k_1 \cos \phi \, B_0 - \frac{\sigma}{\sigma_1}(1 - A_0) k \cos \theta \right\}, \tag{70}$$

$$\frac{\sigma}{\sigma_1} A'_n - B'_n = i\zeta_{-n} \left\{ k_1 \cos \phi \, B_0 - \frac{\sigma}{\sigma_1}(1 - A_0) k \cos \theta \right\}. \tag{71}$$

In forming the second boundary condition (67) we require in $d(\psi - \psi_1)/dx$ only the part independent of ζ. Thus

$$\frac{d(\psi - \psi_1)}{dx} = ik \sin \theta \, e^{ikx \sin \theta} \{1 + A_0 - B_0\}.$$

Also

$$e^{-ikx \sin \theta} \frac{d\psi}{dz} = ik \cos \theta \left\{ 1 - A_0 + (1 + A_0) ik\zeta \cos \theta \right\}$$

$$- ik \cos \theta_n A_n \, e^{inpx} - ik \cos \theta'_n A'_n \, e^{-inpx},$$

$$e^{-ikx \sin \theta} \frac{d\psi_1}{dz} = ik_1 \cos \phi \, B_0 (1 + ik_1 \zeta \cos \phi)$$

$$+ ik_1 \cos \phi_n B_n \, e^{inpx} + ik_1 \cos \phi'_n B'_n \, e^{-inpx}.$$

Thus (67) takes the form

$$ik \cos \theta \, (1 - A_0) - ik_1 \cos \phi \, B_0 \qquad ,$$

$$- k^2 \cos^2 \theta \, (1 + A_0) \, \zeta + k_1^2 \cos^2 \phi \, B_0 \, \zeta$$

$$- e^{inpx} \left\{ ik \cos \theta_n A_n + ik_1 \cos \phi_n B_n \right\}$$

$$- e^{-inpx} \left\{ ik \cos \theta'_n A'_n + ik_1 \cos \phi'_n B'_n \right\}$$

$$= ik \sin \theta \, (1 + A_0 - B_0) \, d\zeta/dx. \tag{72}$$

From the part independent of x we get

$$k \cos \theta \, (1 - A_0) - k_1 \cos \phi \, B_0 = 0, \tag{73}$$

and from the parts in e^{inpx}, e^{-inpx}

$$k \cos \theta_n A_n + k_1 \cos \phi_n B_n = i\zeta_n \left\{ k^2 \cos^2 \theta \, (1 + A_0) - k_1^2 \cos^2 \phi \, B_0 \right.$$
$$\left. - npk \sin \theta \, (1 + A_0 - B_0) \right\}, \tag{74}$$

and a similar equation involving A'_n, B'_n.

From (69), (73) we find

$$A_0 = \frac{\dfrac{\sigma_1}{\sigma} - \dfrac{\cot \phi}{\cot \theta}}{\dfrac{\sigma_1}{\sigma} + \dfrac{\cot \phi}{\cot \theta}}, \qquad B_0 = \frac{2}{\dfrac{\sigma_1}{\sigma} + \dfrac{\cot \phi}{\cot \theta}}. \tag{75}$$

Again, eliminating B_n between (70), (74), we get, with use of (5),

$$A_n \{k \cos \theta_n + k_1 \cos \phi_n \cdot \sigma/\sigma_1\}$$

$$= \frac{2ik^2\zeta_n}{D}\left[\frac{\sigma_1}{\sigma}\cos^2\theta - \frac{\sigma_1-\sigma}{\sigma}\frac{np}{k}\sin\theta \right.$$

$$\left. -\frac{\sin^2\theta\cos\phi}{\sin^2\phi}\left\{\cos\phi - \cos\phi_n + \frac{\sigma}{\sigma_1}\cos\phi_n\right\}\right], \qquad (76)$$

D denoting the denominators in (75).

The equations (75) for the waves regularly reflected and refracted are those given (after Green) in 'Theory of Sound,' § 270. They are sufficiently general to cover the case where the two gaseous media have different constants of compressibility (m, m_1) as well as of density (σ, σ_1). The velocities of wave propagation are connected with these quantities by the relation, see (5),

$$k_1^2 : k^2 = \sin^2\theta : \sin^2\phi = V^2 : V_1^2 = m/\sigma : m_1/\sigma_1. \qquad (77)$$

In ideal gases the compressibilities are the same, so that

$$\sigma_1 : \sigma = \sin^2\theta : \sin^2\phi. \qquad (78)$$

In this case (75) gives

$$A_0 = \frac{\sin 2\theta - \sin 2\phi}{\sin 2\theta + \sin 2\phi} = \frac{\tan(\theta-\phi)}{\tan(\theta+\phi)}, \qquad (79)$$

Fresnel's expression for the reflection of light polarised in a plane perpendicular to that of incidence. In accordance with Brewster's law the reflection vanishes at the angle of incidence whose tangent is V/V_1.

In like manner the introduction of (78) into (76) gives, after reduction,

$$A_n \{k \cos \theta_n + k_1 \cos \phi_n \cdot \sigma/\sigma_1\}$$

$$= 2ik^2\zeta_n \cot \theta \tan(\theta-\phi) \{\cos(\theta+\phi)\cos(\theta-\phi)$$

$$-\cos\phi (\cos\phi - \cos\phi_n) - np/k \cdot \sin\theta\}. \qquad (80)$$

If the wave-length of the corrugations be very long, $p = 0$, $\cos\phi_n$ becomes identical with $\cos\phi$, and thus A_n vanishes when $\cos(\theta+\phi) = 0$, that is at the same (Brewsterian) angle of incidence for which $A_0 = 0$, as was to be expected. In general $A_n = 0$, when

$$\cos(\theta+\phi)\cos(\theta-\phi) = \cos\phi(\cos\phi - \cos\phi_n) + np/k \cdot \sin\theta. \qquad (81)$$

If we suppose that np/k is somewhat small, we may obtain a second approximation to the value of $\cos(\theta+\phi)$. Thus, setting in the small terms $\theta+\phi = \frac{1}{2}\pi$, we get

$$\cos(\theta+\phi) = \frac{1}{2}\sec\theta \{\cos\phi - \cos\phi_n + np/k\}.$$

Here $\cos \phi_n = \cos \phi - np/k_1 . \tan \phi = \cos \phi - np/k . \cot^2 \theta,$

so that $$\cos (\theta + \phi) = \frac{np}{2k \sin^2 \theta \cos \theta} . \tag{82}$$

This determines the angle of incidence at which to a second approximation (in np/k) the reflected vibration vanishes in the nth spectrum.

Since according to (82) with n positive $\theta + \phi < \frac{1}{2}\pi$, and $\theta_n > \theta$, it seemed not impossible that (82) might be equivalent to $\cos (\theta_n + \phi) = 0$, forming a kind of extension of Brewster's law. It appears, however, from (6) that

$$\cos (\theta_n + \phi) = \frac{np}{k \cos \theta} \left(\frac{1}{2 \sin^2 \theta} - 1 \right), \tag{83}$$

so that the suggested law is not observed, although the departure from it would be somewhat small in the case of moderately refractive media.

For the other spectrum of the nth order we have only to change the sign of n in (82), (83).

When np/k is not small, we must revert to the original equation (81). Even this, it must be remembered, depends upon a first approximation, including only the first powers of the ζ's.

Another special case of interest occurs when $\sigma_1 = \sigma$, so that in the acoustical application the difference between the two media is one of compressibility only. The introduction of this condition into (75) gives

$$A_0 = \frac{\tan \phi - \tan \theta}{\tan \phi + \tan \theta} = \frac{\sin (\phi - \theta)}{\sin (\phi + \theta)}, \tag{84}$$

the other Fresnel's expression.

Again, from (76),

$$A_n \{k \cos \theta_n + k_1 \cos \phi_n\} = \frac{2ik^3\zeta_n}{D} \left\{ \cos^2 \theta - \frac{\sin^2 \theta \cos^2 \phi}{\sin^2 \phi} \right\},$$

whence $$A_n = \frac{2ik\zeta_n \cos \theta \sin (\phi - \theta)}{\sin \phi \cos \theta_n + \sin \theta \cos \phi_n}. \tag{85}$$

In this case the vibration in the nth spectrum does not vanish at any angle of incidence.

We have now to consider the application of our solutions to electromagnetic vibrations, such as constitute light, the polarisation being in one or other principal plane. In the usual electrical notation,

$$V^2 = 1/K\mu, \qquad V_1^2 = 1/K_1\mu_1,$$

K. K_1 being the specific inductive capacities, and μ, μ_1 the magnetic permeabilities : while in the acoustical problem,

$$V^2 = m/\sigma, \qquad V_1^2 = m_1/\sigma_1.$$

The boundary conditions are also of the same general form. For instance, the acoustical conditions

$$\sigma \psi = \sigma_1 \psi_1, \qquad d\psi/dn = d\psi_1/dn,$$

may be written

$$(\sigma \psi) = (\sigma_1 \psi_1), \qquad \sigma^{-1} d(\sigma \psi)\, dn = \sigma_1^{-1} d(\sigma_1 \psi_1)/dn;$$

and in the upper medium where σ is constant it makes no difference whether we deal with ψ or $\sigma \psi$. Thus if in the case of light we identify ψ with β, the component of magnetic force parallel to y, the conditions to be satisfied at the surface are the continuity of β and of $K^{-1} d\beta/dn$.[*]

Comparing with the acoustical conditions, we see that K replaces σ, and consequently (by the value of V^2) μ replaces $1/m$. Hence, in the general solution (75), (76), it is only necessary to write K in place of σ. For optical purposes we may usually treat μ as constant. This corresponds to the special supposition (78), so that (79), (80) apply to light for which the magnetic force is parallel to the lines of the grating, or the electric force perpendicular to the lines, *i.e.*, in the plane of incidence.

From (76) we may fall back upon (48) by making $K_1 = \infty$, $\mu_1 = 0$, in such a way that V_1, and therefore ϕ, remains finite.

The other optical application depends upon identifying ψ with Q, the electromotive intensity parallel to y, *i.e.*, parallel to the lines of the grating. The conditions at the surface are now the continuity of Q and of $\mu^{-1} dQ/dn$. Equations (75), (76) become applicable if we replace σ by μ. If μ be invariable, this is the special case of (84), (85); so that these equations are applicable to light when the electric vibration is parallel to the lines of the grating, or perpendicular to the plane of incidence. The associated Fresnel's expression (79) or (84) suffices in each case to remind us of the optical circumstances.

In order to pass back from (76) to (13), we are to suppose $K_1 = \infty$, μ_1 (or σ_1) $= 0$, so that ϕ remains finite. Thus $D = \cot \phi/\cot \theta$, and the only terms to be retained in (76) are those which include the factor σ/σ_1.

The polarisation of the spectra reflected from glass gratings was noticed by Fraunhofer:— " Sehr merkwürdig ist es, dass unter einem gewissen Einfallswinkel ein Theil eines durch Reflexion entstandenen Spectrums aus *vollständig polarisirtem Lichte* besteht. Dieser Einfallswinkel ist für die verschiedenen Spectra sehr verschieden, und selbst noch sehr merklich für die verschiedenen Farben ein und desselben Spectrums. Mit dem Glasgitter $\epsilon = 0\cdot0001223$ ist polarisirt: E ($+$ I), *d. i.*, der *grüne* Theil dieses ersten

[*] See 'Phil. Mag.,' vol. 12, p. 81, 1881 ; 'Scientific Papers,' vol. 1, p. 520.

Spectrums, wenn $\sigma = 49°$ ist; E(+II), oder der grüne Theil in dem zweiten auf derselben Seite der Axe liegenden Spectrum, wenn $\sigma = 40°$ beträgt; endlich E (—I), oder der grüne Theil des ersten auf der entgegengesetzten Seite der Axe liegenden Spectrums, wenn $\sigma = 69°$. Wenn E(+ I) vollständig polarisirt ist, sind es die übrigen Farben dieses Spectrums noch unvollständig."[*]

In Fraunhofer's notation σ is the angle of incidence, here denoted by θ, and λ (E) $= 0·00001945$ in the same measure (the Paris inch) as that employed for ϵ, so that $p/k = \lambda/\epsilon = 0·159$. If we suppose that the refractive index of the glass was 1·5, we get

Order.	θ.	Sin θ.	Sin ϕ.	ϕ.	$\theta + \phi$.
	°			° ′	° ′
E (+I)	49	0·755	0·503	30 11	79 11
E (+II)	40	0·643	0·429	25 25	65 25
E (—I)	69	0·934	0·623	107 33	107 33

On the other hand, from (82) we get for E(+I) $\theta + \phi = 77° \ 44'$, for E(+II) $59° \ 48'$, and E(—I) $104° \ 45'$, a fair agreement between the two values of $\theta + \phi$, except in the case of E (+II).

It appears, however, that the neglect of p^2 upon which (82) is founded is too rough a procedure. By trial and error I calculate from (81) for E(+I) $\theta = 48° \ 52'$; for E(+II) $\theta = 42° \ 17'$; for E(—I) $\theta = 65° \ 46'$. These agree perhaps as closely as could be expected with the observed values, considering that they are deduced from a theory which neglects the square of the depth of the ruling. The ordinary polarising angle for this index (1·5) is $56° \ 19'$.

It would be of interest to extend Fraunhofer's observations; but the work should be in the hands of one who is in a position to rule gratings himself. On old and deteriorated glass surfaces polarisation phenomena are liable to irregularities.

In the hope of throwing light upon the remarkable observation of Professor Wood,[†] that a frilled collodion surface shows an enhanced reflection, I have pursued the calculation of the regularly reflected light to the second order in ζ, the depth of the groove, limiting myself, however, to the case of perpendicular incidence and to the supposition that ζ_1 and its equal

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[*] Gilbert's 'Ann. d. Physik,' vol. 74, p. 337 (1823); 'Collected Writings,' Munich, 1888, p. 134.

[†] 'Physical Optics,' p. 145.

ζ_{-1} are alone sensible. Although the results are not what I had hoped, it may be worth while to record the principal steps.

Retaining only the terms independent of x, we get from the first condition (65),

$$\sigma/\sigma_1 \cdot \{(1+A_0)(1-k^2\zeta_1^2)-2ik\zeta_1\cos\theta_1 A_1\} = B_0(1-k_1^2\zeta_1^2)+2ik_1\zeta_1\cos\phi_1 B_1,$$
$$(86)$$

and from the second condition (67),

$$k(1-A_0)(1-k^2\zeta_1^2)+2ik^2\zeta_1 A_1\cos^2\theta_1-k_1 B_0(1-k_1^2\zeta_1^2)-2ik_1^2\zeta_1 B_1\cos^2\phi_1$$
$$= -2ip^2\zeta_1(A_1-B_1). \qquad (87)$$

Eliminating $B_0(1-k_1^2\zeta_1^2)$, and remembering that

$$k^2\cos^2\theta_1+p^2 = k^2, \qquad k_1^2\cos^2\phi_1+p^2 = k_1^2,$$

we get

$$k(1-A_0)-\sigma/\sigma_1 \cdot k_1(1+A_0)+2ik^2\zeta_1 A_1$$
$$+\sigma/\sigma_1 \cdot 2ikk_1\zeta_1 A_1\cos\theta_1+2ik_1^2\zeta_1 B_1\cos\phi_1-2ik_1^2\zeta_1 B_1 = 0, \qquad (88)$$

in which we are to substitute the values of A_1, B_1 from (70), (74). From this point it is, perhaps, more convenient to take the principal suppositions separately.

Let, as in (78), $\sigma_1 : \sigma = \sin^2\theta : \sin^2\phi = k_1^2 : k^2$;

we have

$$A_0 = \frac{k_1-k}{k_1+k}, \qquad B_0 = \frac{2k^2}{k_1(k_1+k)},$$

and accordingly, from (70), (74),

$$k^2A_1-k_1^2B_1 = 2ik^2\zeta_1(k_1-k), \quad k\cos\theta_1 A_1+k_1\cos\phi_1 B_1 = 0;$$

so that $A_1\{k\cos\phi_1+k_1\cos\theta_1\} = 2ik\zeta_1(k_1-k)\cos\phi_1.$

Hence, from (88),

$$\frac{1-A_0}{1+A_0} = \frac{k}{k_1}+\frac{2k\zeta_1^2(k_1^2-k^2)}{k_1}\left\{1-\frac{(k_1^2-k^2)\cos\theta_1\cos\phi_1}{k_1(k\cos\phi_1+k_1\cos\theta_1)}\right\}. \qquad (89)$$

Again, when $\sigma_1 = \sigma$,

$$A_0 = \frac{k-k_1}{k+k_1}, \qquad B_0 = \frac{2k}{k+k_1}$$

and from (70), (74),

$$A_1 = B_1 = \frac{2ik\zeta_1(k-k_1)}{k\cos\theta_1+k_1\cos\phi_1}. \qquad (90)$$

The introduction of these into (88) gives

$$\frac{1-A_0}{1+A_0} = \frac{k_1}{k} - \frac{2(k_1^2-k^2)\zeta_1^2}{k}\left\{k_1-\frac{k_1^2-k^2}{k\cos\theta_1+k_1\cos\phi_1}\right\}. \qquad (91)$$

The question is whether the numerical value of A_0 is increased or diminished by the term in ζ_1^2. In (89) it is easy to recognise that in the standard case of k_1 greater than k (air to glass in optics) the term in ζ_1^2 is positive, θ_1 and ϕ_1 being supposed real. The effect of the second term is thus to bring the right-hand member nearer to unity than it would otherwise be, and thus to *diminish* the reflection. Again, in (91), the second term is negative, even when $\cos\theta_1 = 0$, as we may see by introducing the appropriate value of $\cos\phi_1$, viz., $\sqrt{(1-k^2/k_1^2)}$. The effect is therefore to subtract something from k_1/k, which is greater than unity, and thus again to diminish the reflection.

If in (89), (91) we neglect the terms in $(k_1^2-k^2)^2\,\zeta_1^2$, which will be specially small when the two media do not differ much, the formulæ become independent of the angles θ_1 and ϕ_1. In both cases the effect is the same as if the refractive index, supposed greater than unity, were diminished in the ratio $1-2\,(k_1^2-k^2)\zeta_1^2:1$. It appears then that the present investigation gives no hint of the enhanced reflection observed in certain cases by Professor Wood.

On the Velocity of Rotation of the Electric Discharge in Gases at Low Pressures in a Radial Magnetic Field.

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The following paper contains an account of a series of experiments on the motion of an electric discharge in a magnetic field perpendicular to the direction of the discharge current. The fact that the discharge moves in a magnetic field like a flexible conductor carrying a current was discovered long ago, and De La Rive showed that it could be made to rotate continuously round one pole of a magnet placed inside the vacuum tube.

The apparatus used in the present experiments was similar in principle to De La Rive's, but was arranged so that fairly exact measurements of the various quantities concerned could be obtained. Fig. 1 shows a vertical section of the vacuum tube and magnet used. The tube consisted of two concentric glass tubes cemented with sealing wax into aluminium discs. The discs had grooves turned in them to fit the glass tubes, and the part of the discs between the tubes projected a few millimetres, so that there was no danger of the discharge passing through the sealing wax. Polished platinum rings were fixed on to the aluminium discs between the glass tubes, and these formed the electrodes between which the discharge was passed. The ends of the tubes were carefully ground truly perpendicular to their axes, and the two platinum rings were accurately parallel. To keep the electrodes cool, a ring of narrow brass tubing was soldered on to the back of each disc and a stream of water was kept flowing through these whenever a discharge was passed. This arrangement enabled comparatively large currents to be used without softening the sealing wax. A narrow copper tube was soldered into one of the discs and communicated with the interior of the vacuum tube through a fine hole. The tube was connected by a mercury sealed joint with a glass tube leading to a bulb containing pure phosphorus pentoxide, a Töpler pump, and a McLeod gauge.

The aluminium discs could be connected through an ammeter and resistance to a battery of 800 secondary cells. The magnet used to produce the magnetic field consisted of a soft iron bar which was magnetised by means of two solenoids, one at each end, so as to have one pole in the middle and opposite poles at each end. The bar was fixed along the axis of the vacuum tube as shown, so that the middle of the bar was at the centre of the tube. The bar was

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surrounded by a closely fitting thin-walled glass tube, which prevented the aluminium discs coming in contact with it.
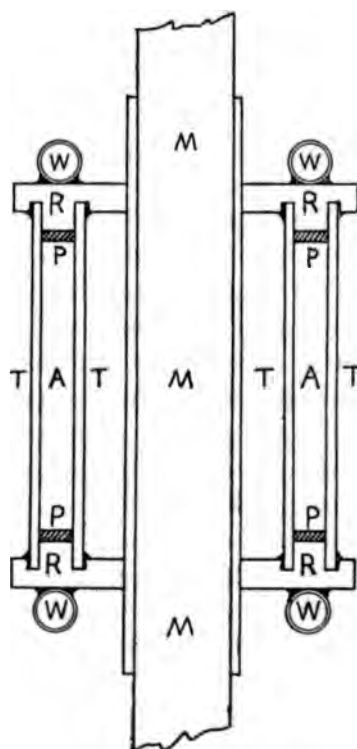
• Fɪɢ. 1.—Vertical section of discharge tube through its axis.

M M M—Iron bar with glass tube round it.	T T T T—Glass tubes.
R R R R—Aluminium rings.	A A—Annular space through which discharge passed.
P P P P—Platinum rings.	W W W W—Water cooling tubes.

The distribution of the magnetic force around the bar in the region occupied by the vacuum tube was investigated by means of a small compass needle and was found to be sensibly radial.

The current through the magnetising solenoids was measured with an accurate ammeter. Before beginning an experiment, the bar was demagnetised by the method of reversals and then the current was slowly increased, with frequent reversals, up to the required value. In this way the effects of permanent magnetism in the bar were eliminated and the magnetic field could be regarded as a definite function of the current.

The strength of the magnetic field corresponding to different values of the current was found by means of a coil of 50 turns of wire, which was

connected to a ballistic galvanometer and placed round the bar magnet in the position usually occupied by the vacuum tube. The deflections of the galvanometer, produced by reversing a series of currents in the solenoids, were found, and then the coil was placed in a solenoid giving a field of known strength, which was then reversed and the galvanometer deflection measured. The coil of 50 turns was wound in two sections in grooves of square cross-section turned on a boxwood circular cylinder, each groove containing 25 turns. The outside diameter of each section was equal to the outside diameter of the annular space between the two glass tubes forming the vacuum tube, and the inside diameters were equal to the inside diameter of the annular space. The distance between the centres of the two sections was equal to the distance between the platinum electrodes. The two sections were first connected together in series, so that a current would pass round them in opposite directions, and the boxwood cylinder was then placed in the position of the vacuum tube on the iron bar and the galvanometer deflections obtained. The two sections were then connected in series, so that a current would pass round them in the same direction, and were placed inside the solenoid so that the axis of the cylinder was parallel to its magnetic field, and the galvanometer deflection due to reversing this field was obtained.

Let S = strength of field due to the solenoid when a current of 1 ampère is passed round it.

C = current reversed in the solenoid.

r = radius of the mean area of each section of the coil of 50 turns.

l = distance between the centres of the two sections.

d = galvanometer swing due to reversing C.

d' = galvanometer swing due to reversing the magnetisation of the iron bar.

F = field due to iron bar at radius r.

Then $Ad = 100 \pi r^2 SC$ and $Ad' = 100 \pi r l F$,

where A is a constant. Hence

$$F = SCrd'/ld.$$

The values of F corresponding to a series of currents in the solenoids for magnetising the bar were found in this way.

The following are the dimensions of the vacuum tube :—

Inside diameter of outside tube	3·01 cm.
Outside diameter of inside tube	2·32 „
Distance between electrodes	3·17 „

The radius of the mean area of each section of the coil used to find the strength of the magnetic field was 1·34 cm., which is nearly equal to the mean radius, 1·33 cm. The magnetic field acting on the discharge is inversely proportional to the radius, so that the parts of the discharge furthest from the axis of the tube are acted on by the weakest field. The fields given in the tables of results are in every case the field at the radius $r = 1·34$ cm.

When a discharge was passed through a gas at a few millimetres pressure it usually formed a narrow positive column perpendicular to the surfaces of the electrodes. The negative glow covered the part of the negative electrode opposite to the end of the positive column and extended over a greater or less area besides, according to the strength of the current. With large currents, the whole of the negative electrode was covered by the negative glow, but even when this was the case the positive column remained quite narrow, usually not more than 1 cm. wide. At low pressures with large currents, the positive column sometimes spread out and extended all round the tube, so that it became impossible to observe the rotation of the discharge when a magnetic field was produced.

When the iron bar was magnetised so as to produce a radial magnetic field through the vacuum tube, the positive column usually began to move rapidly round the annular space between the electrodes. The negative glow went round with the positive column unless it covered the whole surface of the electrode, in which case it was impossible to tell whether it went round or not.

The number of revolutions per second was found by observing the discharge through a stroboscopic disc driven by an electric motor. The speed of rotation of the disc was measured with a revolution counter, which was usually kept on for 30 seconds at a time. The disc had several concentric rings of holes bored in it and its speed was adjusted so that the discharge as seen through it appeared to remain at rest in one of the circles of holes. In this way it was usually easy to get the number of revolutions per second made by the discharge in terms of the number made by the disc. With a weak magnetic field the rotation was sometimes slow enough for the revolutions to be directly counted.

At low pressures with strong fields the speed sometimes was several hundred revolutions per second, and it was rather difficult to be quite sure of the relation between the speed of the disc and the speed of the discharge. In such cases several independent determinations were made, using different speeds for the disc. When the way in which the speed depends on the magnetic field and gas pressure had been found, it was possible to calculate roughly what the speed might be expected to be in a particular case, so that

it became easy to find the correct factor required to convert the speed of the disc into the speed of the discharge.

When a weak magnetic field was turned on, the discharge sometimes did not start revolving, but appeared to stick at one of the electrodes (usually the cathode) and was bent into the shape of a screw round the discharge tube. The screw usually did not make more than a fraction of a turn round the tube. On increasing the field slowly, the discharge suddenly began to rotate, and then, on diminishing the field, would continue rotating with a much smaller field than was necessary to start it. When rotating rapidly, the discharge as seen in the stroboscope appeared exactly as it appeared when at rest without any field, and was always perpendicular to the electrodes. An exception to this rule was observed in the case of hydrogen at low pressures, when the positive column sometimes became broader when set rotating and sometimes split up into two separate columns diametrically opposite each other, which always coalesced on turning off the field.

The rotation of the discharge in air, nitrogen, and hydrogen was examined. The air was passed over solid caustic potash and dried with phosphorus pentoxide. The nitrogen was prepared by the action of pure urea on potassium hypobromite and was passed over caustic potash, calcium chloride, and phosphorus pentoxide; it appeared to be pure and did not act on the mercury in the pump. The hydrogen was prepared by the action of pure hydrochloric acid on pure zinc, and was passed over caustic potash, calcium chloride, and phosphorus pentoxide. The spectrum of the discharge was observed in each case through a large direct-vision spectroscope and appeared to be that of the gas supposed to be present. The most complete set of results was obtained with nitrogen; hydrogen was found difficult to work with, except at high pressures.

The Rotation of the Discharge in Nitrogen.

The following table (page 422) gives some of the results obtained, showing the variation of the velocity of rotation with the magnetic field at several pressures.

Magnetic field. H.	Revolutions per sec. *n*.	*n*/H.	Magnetic field. H.	Revolutions per sec. *n*.	*n*/H.
	Pressure 10·3 mm.			Pressure 4·35 mm.	
41	9·5	0·23	27	11·5	0·43
59	13·9	0·24	46	20·0	0·44
74	19·0	0·26	51	27·0	0·53
96	23·7	0·25	59	32·0	0·54
121	31·3	0·26	73	43·0	0·59
134	35·9	0·27	88	59·0	0·67
			109	88·0	0·81
		Mean 0·25			Mean 0·57
	Pressure 7·0 mm.			Pressure 11·4 mm.	
41	14·9	0·36	31	6·4	0·21
59	20·5	0·35	40	9·0	0·22
74	26·9	0·36	78	16·1	0·21
98	37·8	0·38	107	25·0	0·23
			133	32·0	0·24
		Mean 0·36			Mean 0·22

It will be seen that, except at the lowest pressure, the velocity of rotation at each pressure is nearly proportional to the magnetic field.

In the following table, the mean values of n/H are given, and the product of n/H and the pressure:—

Pressure p.	n/H.	np/H.
11·4	0·22	2·50
10·3	0·25	2·57
7·0	0·36	2·52
4·35	0·57	2·48

The product np/H is nearly constant, so that the number of revolutions per second (n) is given approximately by the equation $n = BH/p$, where $B = 2·5$.

In all the above experiments the currents carried by the discharge were between 10^{-2} and 3×10^{-2} ampère. A number of measurements were made to find how the velocity varied with the current. The results obtained can be best exhibited by means of curves. Fig. 2 shows a typical curve representing a series of observations at constant pressure and with a constant magnetic field.

It will be seen that the velocity of rotation passes through a very flat minimum value as the current is varied. The numbers given above on the variation of the velocity with the pressure and the field are for currents lying in the range for which the velocity is nearly independent of the
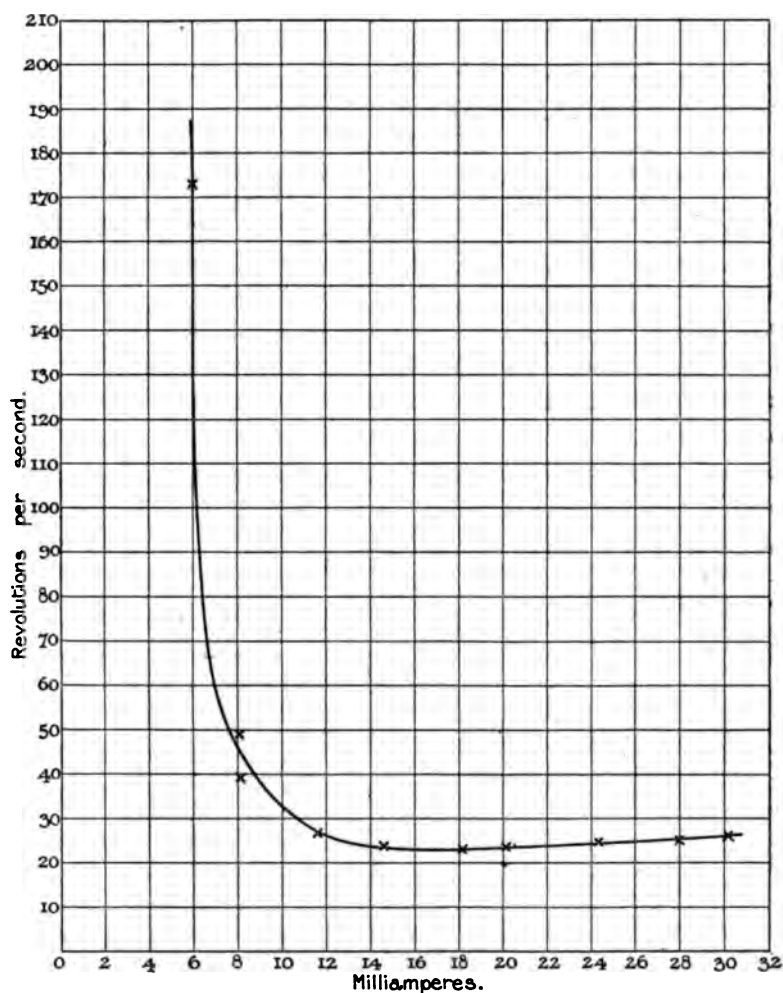
Fig. 2.—Magnetic field 41. Pressure 2·8 mm.

current. The velocity appeared to be nearly proportional to the magnetic field under any conditions, but when the velocity varied rapidly with the current it was difficult to obtain satisfactory measurements, because of the difficulty of keeping the current exactly constant.

The Velocity of Rotation in Air and in Hydrogen.

Similar results were obtained with air to those obtained with nitrogen. The following table contains some of them :—

p.	n.	H.	np/H.
4·7	19·5	34	2·7
4·7	42·2	73	2·5
8·0	14·7	40	2·9
8·0	29·1	85	2·7
11·8	22·1	88	3·0
			Mean 2·8

It will be seen that np/H is nearly constant, so that, for air, $n = 2·8$H/p and so does not differ much from n in nitrogen. The rapid variation of n with the current observed with nitrogen when the current was small was not observed with air.

In the case of hydrogen, the ranges of current and pressure over which it was possible to make observations were rather limited. The following table contains some of the results obtained :—

p.	n.	H.	np/H.
6·5	220	43	33
6·5	480	91	34
6·5	670	133	33
6·5	780	164	31
9·1	370	107	31
9·1	475	133	33
			Mean 32·5

Thus, for hydrogen, $n = 32·5$ H/p, and so is about 13 times greater than in nitrogen. The velocity seems, therefore, to be inversely as the density of the gas.

The numbers given above refer to the number of revolutions per second made by the discharge. For purposes of theoretical calculation it is more convenient to express the results in terms of the velocity of motion of the discharge in centimetres per second. Since the mean radius of the discharge tube was 1·33 cm., the revolutions per second must be multiplied by $2\pi \times 1·33 = 8·36$. If u denotes the velocity, we have, then, for nitrogen, $u = 20·9$ H/p; for air, $u = 23·4$ H/p; and for hydrogen, $u = 272$ H/p.

Theory of the Rotation of the Discharge.

The quantity observed was the velocity of rotation of the positive column of the discharge. In many of the experiments the negative glow covered the whole surface of the negative electrode and so could not be observed to rotate. Very often the positive column was striated when at rest, and remained so when rotating without any change in its appearance as seen through the stroboscopic disc. To simplify the theory, we shall suppose the discharge to be uniform and to be moving perpendicular to itself in a uniform magnetic field of strength H. If C denote the current carried by the discharge, then the transverse force per centimetre acting on the discharge is HC. If we suppose that this force is balanced by the resistance to the motion of the positive and negative ions through the gas, we get $HC = u (A_1N_1 + A_2N_2)$, where u denotes the transverse velocity of the discharge, A_1 and A_2 denote the resistances to the motion of one positive and one negative ion respectively when moving with unit velocity, and N_1 and N_2 denote the numbers of positive and negative ions present per centimetre of the discharge. If X denotes the electric intensity along the discharge, then

$$C = eX (k_1N_1 + k_2N_2),$$

where e is the charge on each ion and k_1 and k_2 are the velocities of the ions due to unit electric intensity. If v_1 and v_2 denote the velocities of the ions along the discharge, then

$$Xe = v_1A_1 \quad \text{and} \quad Xe = v_2A_2,$$

also $\qquad\qquad v_1 = k_1X \quad \text{and} \quad v_2 = k_2X,$

so that $\qquad\quad A_1 = e/k_1 \quad \text{and} \quad A_2 = e/k_2.$

Hence $\qquad\qquad HC = eu (N_1/k_1 + N_2/k_2).$

Therefore $\quad HX (k_1N_1 + k_2N_2) = u (N_1/k_1 + N_2/k_2),$

and, if we assume $N_1 = N_2$, we get

$$u = HXk_1k_2, \quad \text{or} \quad u = \frac{H}{X} v_1v_2.$$

The Hall effect in the positive column in several gases was measured by one of us in 1901,[*] and it was shown that if Z is the transverse electric intensity due to the Hall effect, then, theoretically; $Z = \frac{1}{2}HX (k_2 - k_1)$, in which Z was found experimentally to be given by the equation $Z = DH/p$, where D is a constant and p the pressure in millimetres of mercury.

Since the velocity of motion of the discharge is given approximately by the

* 'Proceedings of the Cambridge Philosophical Society,' vol. 11, Parts IV and V.

equation $u = CH/p$, it follows that the Hall effect should be proportional to the velocity of motion. We have—

$$u = C\frac{H}{p} = HXk_1k_2 \quad \text{and} \quad Z = D\frac{H}{p} = \tfrac{1}{2}HX\,(k_2 - k_1),$$

so that $\qquad\qquad C = pXk_1k_2 \quad \text{and} \quad 2D = pX\,(k_2 - k_1).$

If X is known, these two equations enable k_2 and k_1 to be calculated.

Unfortunately, there is considerable uncertainty about the value of X. X falls off as the current density is increased ; and the current density in the experiments on the rate of motion of the discharge was considerably greater than in the experiments on the Hall effect. Further, the measurements of the Hall effect were made at lower pressures than those on the velocity of rotation, and it is probable that the formula $Z = DH/p$ is only an approximation to the truth, so that extrapolation is not allowable. We have, therefore, only calculated k_2 and k_1 for each gas at the pressure intermediate between the lowest pressure at which the velocity was measured and the highest pressure at which the Hall effect was measured, so reducing the extrapolation as much as possible.

The following table contains the results of this calculation :—

Gas.	D.	C.	p. Millimetres of Hg.	X. Volts per cm.	k_2. cm. per sec. per volt/cm.	k_1. cm. per sec. per volt/cm.
Air	0·0248	23·4	3·8	68	19,700	450
Hydrogen ...	0·0205	272·0	3·8	55	25,000	5000

If we assume that the velocity of the positive ion varies inversely as the pressure, we get, at 760 mm., for air, $k_1 = 2\cdot2$ cm./sec., and for hydrogen, $k_1 = 25$ cm./sec. According to Zeleny, the velocity of the positive ions produced in air at 760 mm. by Röntgen rays is 1·4 cm./sec. for air and 6·7 cm./sec. for hydrogen.

Mr. Aston[*] has calculated k_1 from the results of measurements on the cathode dark space at pressures below 0·5 mm., and his results, calculated to 760 mm., are 0·78 for air and 7·7 for hydrogen. It seems probable, therefore, that $k_1 p$ does not vary much with the pressure. The above results show that k_2 is much larger than k_1 at low pressures, which probably means that some of the negative ions are free electrons.

If the empirical formulæ obtained for the Hall effect and for the velocity of motion are both assumed to apply at pressures below 3·8 mm., and k_1 and

* 'Roy. Soc. Proc.,' A, vol. 79, p. 80.

k_2 calculated, it is found that k_1 is nearly independent of the pressure, while k_2 rises rapidly with diminishing pressure.

The highest pressure at which the Hall effect in air was measured was 2·9 mm., and the lowest pressure at which the velocity of motion was measured was 4·7 mm., so that for 3·8 mm. the calculation of k_2 and k_1 is fairly reliable, but it is certainly not justifiable to use the formula for the velocity of motion below this pressure, or that for the Hall effect above it.

In the case of hydrogen, the Hall effect was not measured above 1 mm., and the velocity not below 6·5 mm., so that very much weight cannot be attached to the values of k_2 and k_1 calculated for hydrogen at 3·8 mm.

If we assume that k_1 is inversely proportional to the pressure at all pressures, then, since $u = CH/p = HXk_1k_2$, we see that k_2X is a constant for all the pressures at which the velocity of motion was measured.

It appears, therefore, that in air between 4·7 and 12 mm., the velocity of the negative ions in the positive column, *i.e.*, k_2X, does not vary much with the pressure.

At low pressures, k_1 is small compared to k_2, so that the Hall effect gives k_2 approximately equal to $2D/pX$, and k_2X varies inversely as the pressure.

At high pressures, X is probably nearly proportional to the pressure, while k_2 is inversely proportional to the pressure, so that k_2X is constant.

On a Standard of Mutual Inductance.

By Albert Campbell, B.A.

CONTENTS.

§ 1. *Introductory.*—In many electrical measurements, such as those of capacity and inductance, as well as in the magnetic testing of iron, an accurately known standard of mutual inductance is of great value. It is sometimes convenient to derive such a standard from the standard unit of resistance, and this may be done in several ways, for example, by the well-known method of the ballistic galvanometer; or by Carey Foster's method the mutual inductions may be tested against a condenser whose capacity has been found in terms of resistance and frequency by Maxwell's commutator method; or it may be obtained directly in similar terms by the help of an unknown inductance by the Hughes-Rayleigh method.

In the National Physical Laboratory I have used both of these latter methods (with the help of a vibration galvanometer) to obtain a working standard of mutual inductance.* But this procedure is somewhat illogical, seeing that the unit of resistance has been itself commonly determined by the aid of mutual inductances calculated from the dimension of the coils or other conductors used; thus for the highest accuracy it is desirable to revert to a standard whose value can be determined solely from the geometrical dimensions. Accordingly, some eighteen months ago, I took in hand the investigation of a suitable design for such a standard, and I proceed to describe the result at which I arrived.

§ 2. *Practical Conditions.*—The most important conditions governing the design were that the standard must be—

(a) accurately calculable from the geometrical dimensions;

(b) as permanent as possible; and

* 'Phys. Soc.,' May, 1907.

(c) of a value sufficiently large to give high sensitivity when used in comparison methods, such as those mentioned above.

In addition to these, it was desirable to keep the resistances of the parts as low as possible and to avoid (as far as possible) the occurrence of eddy currents, and also of capacity effects between the primary and secondary circuits. As is so often the case in designs, a compromise had to be effected between the various conditions, and so it was decided to make the value approximately 0·01 henry.

In order to carry out some of the above conditions, it is clearly desirable that the distance from the primary circuit to the secondary should, for all points, be relatively as great as possible. For convenience, let us call the circuit with the smaller number (n_1) of turns the primary, the secondary having n_2 turns, and let M be the mutual inductance in millihenries. Since M, for a given geometrical disposition of the circuits, is proportional to $n_1 n_2$, a little consideration showed that for M = 10 millihenries it would be desirable to make $n_1 n_2$ of the order of 100,000. Now it seems to be generally recognised that, for a coil whose dimensions have to be accurately measured, the satisfactory construction is of bare wire wound in an accurate screw-cut on a marble cylinder. If the above conditions be kept in mind, it is out of the question, with $n_1 n_2$ = 100,000, to attempt to construct both the primary and secondary circuits of single-layer coils.

As will be shown later, the solution of the problem consists in making the primary an accurately measured single-layer coil or coils, while the secondary is a many-layered coil, *so designed that its dimensions and position do not require to be very accurately determined.* The possibility of such a design and the method of carrying it out were found by an examination of the manner in which M varies with the dimensions and positions of the primary and secondary coils.

I proceed to give some of the more interesting results of this examination.

§ 3. *Variation of* M *with Dimensions and Positions of the Coils.*—First, let us consider the simple case of two circular co-axial coils with winding of negligible section, assuming for convenience of calculation $n_1 n_2$ = 100,000. Let their radii be A and a, and let b be the distance between their centres.

Let $\quad k = 2\sqrt{Aa}/\sqrt{(A+a)^2 + b^2} = \sin \gamma, \quad$ and $\quad k' = \cos \gamma.$

Then* (in henries)

$$M = -4\pi n_1 n_2 \sqrt{Aa} \left\{ \left(k - \frac{2}{k}\right) F_1 + \frac{2}{k} E_1 \right\} 10^{-9}, \qquad (1)$$

where E_1 and F_1 are complete elliptic integrals to modulus k.

* Maxwell's 'Elect. and Mag.,' vol. 2, § 701.

Since
$$\frac{d E_1}{dk} = \frac{1}{k}(E_1 - F_2),$$

and
$$\frac{d F_1}{dk} = \frac{1}{kk'}(E_1 - k'^2 F_1),$$

it can be shown that

$$\frac{\partial M}{\partial a} = \frac{2\pi n_1 n_2}{\sqrt{(A+a)^2+b^2}}\left\{2a\,(F_1 - E_1)+(A-a)\left(\frac{k}{k'}\right)^2 E_1\right\}10^{-9}. \tag{2}$$

From equation (1), mainly by the help of Lord Rayleigh's table,* and in some cases by Nagaoka's formula and tables,† were calculated sets of values of M for a fixed value of A (viz., 10 cm.), and varying values of a and b.

From these calculations the families of curves shown in figs. 1 and 2 were drawn. Each curve in fig. 1 corresponds to a constant value of a, and in
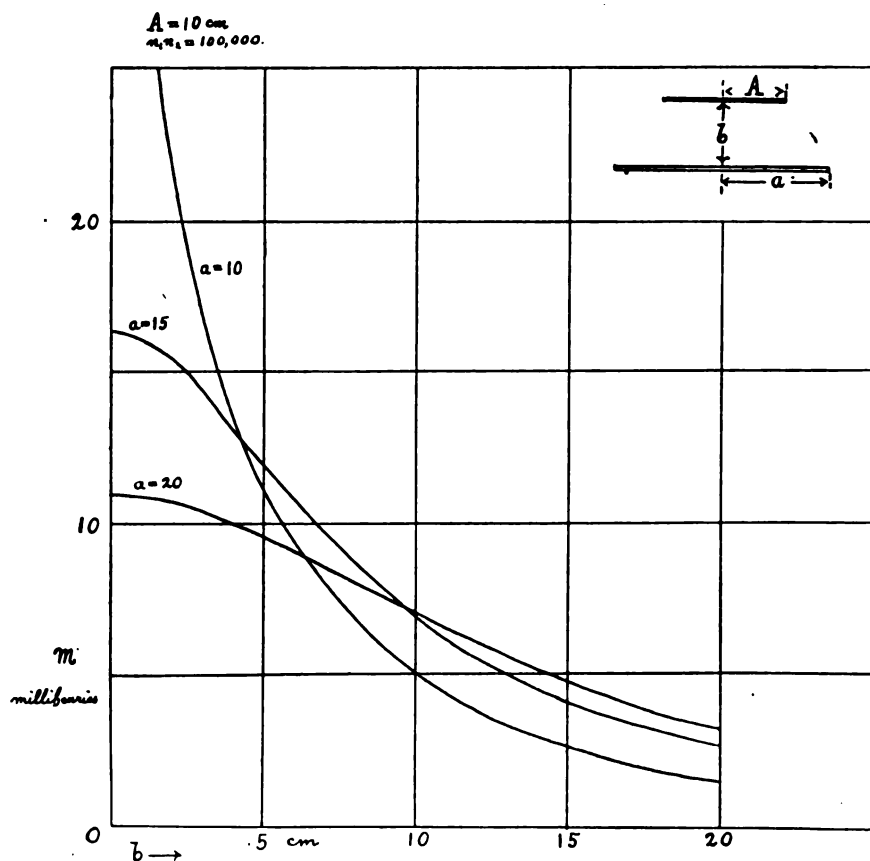
Fig. 1.

* Ibid., 2nd edition.

† Tôkyô Sûg, 'Butsu. Kiji-gaiyo,' vol 2, No. 17.

fig. 2 to a constant value of b. It will be noticed that in fig. 1 M is always maximum (and $\partial M/\partial b = 0$) only when $b = 0$, while in fig. 2 the maximum value occurs for a different value of a (not zero) for each curve. Thus when only two coils are used, b should either be zero or relatively large. When b is zero, $\partial M/\partial a$ is zero only when $a = A$ or the coils coincide; when b is relatively large, the whole construction has to be very bulky in order to obtain a large enough M. Accordingly the case of two coils is not sufficient for our purpose.
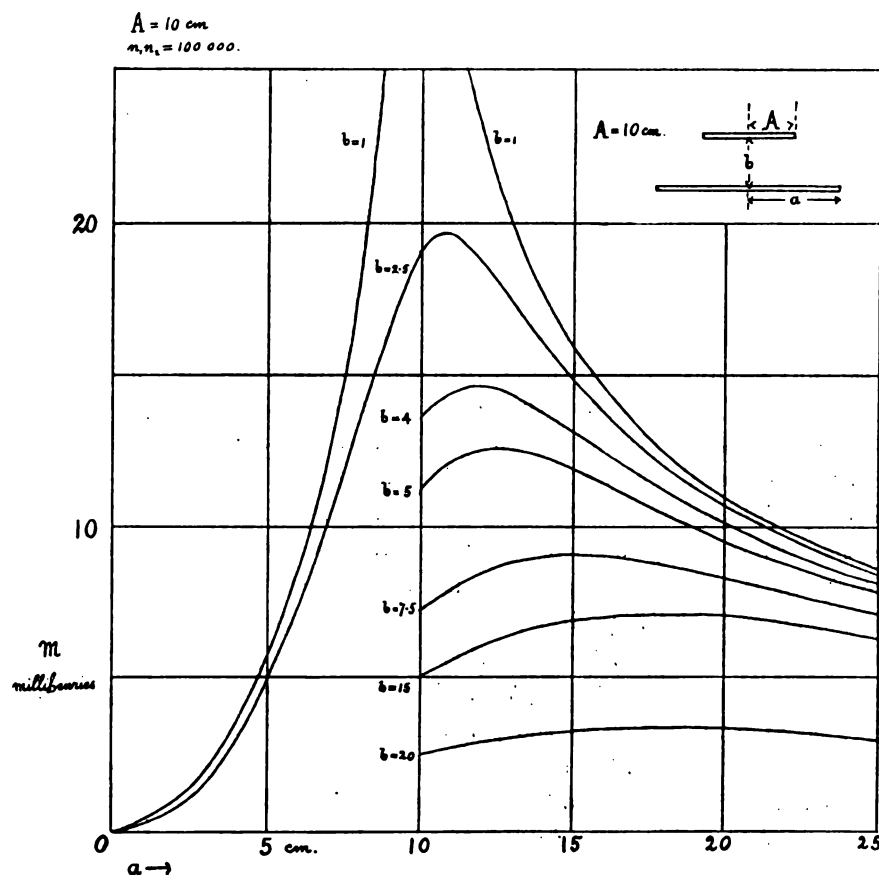
FIG. 2.

If, however, the primary consists of two equal coils arranged with the secondary between them as in fig. 3, all three being coaxial, M is a maximum or minimum for axial displacements when $b_1 = b_2$.

If, then, for any desired value of b ($= b_1 = b_2$) we choose from the proper curve in fig. 2 the value of a which gives M a maximum, the mutual inductance thus obtained varies only very slightly for small variations of a

or small axial displacements of the centre coil; in fact, we have placed the secondary coil in such a position that all round its mean circumference *the field due to the primary coils is zero.*
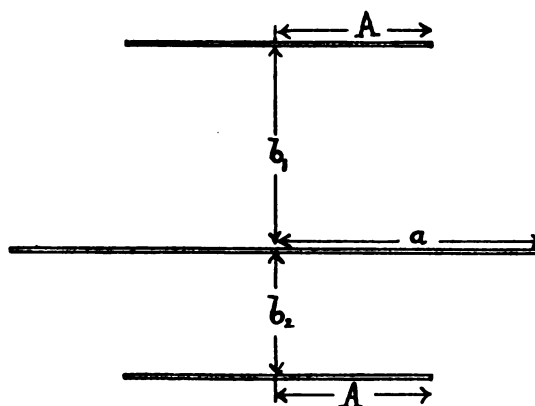
Fig. 3.

If b be chosen of such a value that the corresponding curve in fig. 2 is reasonably flat at its highest point, then the mutual inductance per turn will be practically constant over the whole section of a secondary coil whose axial and radial depths are both small; and the secondary may consist of a many-layered coil whose dimensions and position need not be known with any high accuracy. By doing this we throw all the burden of accuracy on the two primary coils which we have assumed to be mere circles. Clearly these must be replaced by single-layer coils of accurately known dimensions and relative position, and so we must extend the above investigation to the more complicated case where the primary consists of two coaxial helixes, of equal and finite length, with the secondary coil midway between them as in fig. 4. Here at the points P and R (and all round the mean circumference of ROP) the field due to the two primaries should be zero, the component lines of force due to the upper and lower helixes being tangential to one another, and in opposite directions as shown.

§ 4. *Helix and Circle.*—Several cases of the system shown in fig. 4 were investigated by means of the curves of fig. 2. The mutual inductance between the helix LN and the circle RP was taken as approximately*

$$\tfrac{1}{6}\,(M_1 + 4M_2 + M_3),$$

where M_1, M_3, and M_2 refer to circles at the ends and middle of the helix; a similar approximation to $\partial M/\partial a$ was also made and a series of curves were

* Merrifield's ' B.A. Report,' 1880.

drawn. The M and the $\partial M/\partial a$ curves for the particular dimensions which proved satisfactory are shown in fig. 5. The relative dimensions (fig. 4)
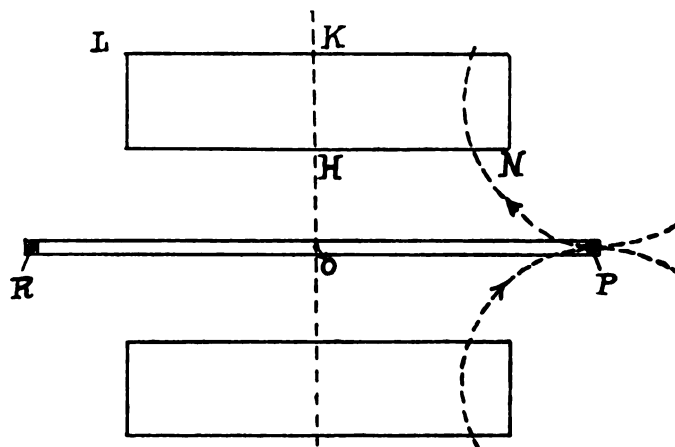
Fig. 4.
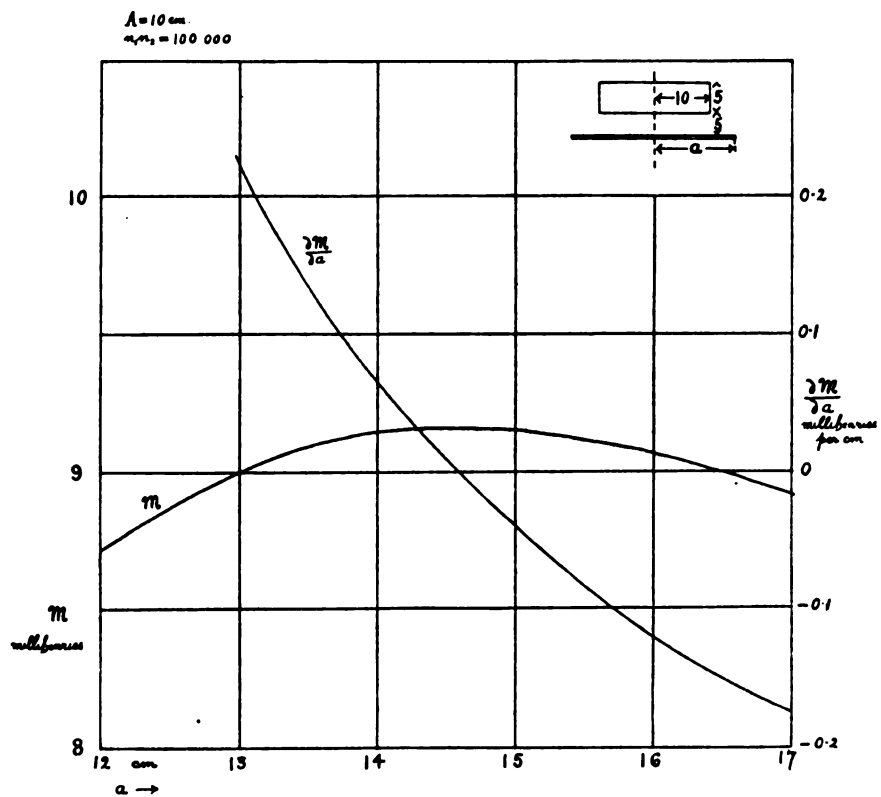
Fig. 5.

are:—HN $=$ A $=$ 10, OH $=$ 5, OK $=$ 10, and OP $=$ 14·60, this last being the value of a for which $\partial M/\partial a = 0$.

It will be noticed that, near the value $a = 14·60$, M shows very little variation with a. (I should mention that the values for M shown in fig. 5 for a single helix and a circle are the same for the two helixes and circle, provided the total number of primary turns be kept constant.)

After the proper relative dimensions had been found by the above method, it was thought desirable to check the results by means of the much more laborious accurate formula of Viriamu Jones.[*] The formula is applied to the helix LN in fig. 4 by calculating for a helix of height OK, and then for one of height OH, and taking the difference.

If
$$c = \frac{2\sqrt{Aa}}{a+A}, \qquad c' = \frac{a-A}{a+A},$$

$$k = \frac{2\sqrt{Aa}}{\sqrt{(a+A)^2+b^2}} = \sin\gamma, \qquad k' = \cos\gamma,$$

and
$$\sin\beta = c'/k',$$

then the Viriamu Jones formula may be reduced to

$$M = 2\times10^{-9}\varpi n_1 n_2 (A+a)\left\{\frac{cF_1(k)-E_1(k)}{k}-\frac{a-A}{b}\Psi\right\}, \qquad (3)$$

where

$$\Psi = -\frac{\varpi}{2}-[F_1(k)-E_1(k)]\,F(k'\beta)+F_1(k)\,E(k'\beta),$$

also
$$\frac{\partial M}{\partial a} = \frac{10^{-9}\varpi n_1 n_2 c}{A}\left\{2AkF_1(k)+\frac{(a+A)^2c}{b}\Psi\right\}. \qquad (4)$$

From (3) were calculated the values of M for A $=$ 10, helix $b = 5$ to 10, with $a = 14·1$, 14·3, 14·5, and 14·7 cm. respectively. The results which are given in the following table entirely corroborate those obtained by the less exact method.

Similarly, formula (4) gave $\partial M/\partial a = 0$ for $a = 14·60$.

Table.—(A $=$ 10, $b = 5$ to 10, $n_1 n_2 = 100,000$.)

a (cm.)	14·1	14·3	14·5	14·7
Millihenries	9·1614	9·1754	9·1762	9·1763

Finally the variation in M due to a small axial displacement of the secondary coil (from the mid position) was estimated. It was found that a displacement of 0·35 cm. reduced M by less than 1 in 10,000.

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[*] ' Roy. Soc. Proc.,' p. 192, December 9, 1897.

It will be seen that, with the above proportions, if the radius of the secondary coil is 14·6 cm., we may make it a coil of many layers and of appreciable cross-section.

If, for example, the cross-section be 0·5 cm. × 0·5 cm., then the maximum variation from the mean value, over the whole section, of the inductance per turn will be the same within a few parts in 1000, and thus we can with perfect safety obtain an accurate result by using a method of averaging, such as the Purkiss formula used by Lord Rayleigh.*

§ 5. *Actual Construction of Standard.*—A standard of the design described above is at present being constructed at the National Physical Laboratory. In this the two primary helixes are of bare wire (75 turns each) wound on one marble cylinder of 30 cm. diameter, while the secondary coil consists of 488 turns in a channel of 1 sq. cm. section with a mean diameter of 43·8 cm., the nominal value, therefore, being close to 10 millihenries.

I may remark that the principle here employed will, without doubt, be of value in other problems where accurately known mutual inductances are required.

In conclusion, I would express my thanks to Dr. R. T. Glazebrook for valued and helpful criticism of the design, and to Mr. F. E. Smith for kind advice with regard to the material construction of it.

* Maxwell's ' Elect. and Mag.,' vol. 2, p. 350, 3rd edition.

On the Origin of the Gases evolved by Mineral Springs.

By the Hon. R. J. STRUTT, F.R.S.

(Received May 31,—Read June 20, 1907.)

It has long been known that thermal springs, such as those at Bath, give off considerable quantities of gas, which bubbles up with the water, and consists, for the most part, of nitrogen. Of recent years interest in this subject has been revived by Lord Rayleigh's observation that helium and argon are present along with nitrogen.[*] Dewar has used the Bath gas as a practical source of helium, and has observed that it contains a trace of neon; more recently, Moureu[†] has exhaustively studied the thermal springs of France, some forty in number, and has found that the same constituents are of quite general occurrence. It appears from his analyses that the Bath gas may fairly be regarded as typical of the gases of almost all other thermal springs, although a much larger percentage of helium is occasionally met with.

It has been found that such gases, when fresh, are rich in radium emanation, and that the deposit thrown down by the water on standing contains a notable quantity of radium. It is natural to connect this observation with the discharge of helium by the springs. I was formerly inclined to think[‡] that the facts were most easily explained by supposing that the supplies of helium and radium were derived from the disintegration of uranium lodes at a great depth by the water; but this view scarcely seems compatible with the universal presence of helium and radium in mineral springs, which has since been brought to light; for uranium lodes are very rare near the earth's surface, and there are fatal objections to supposing that metal to be generally more abundant at greater depths.[§]

The unexpectedly large quantities of radium found in common rocks[||] led me to suspect that perhaps they might after all be able to supply the helium and radium products, as well as the ordinary gases and saline constituents of the spring. With a view to deciding this question, I have examined the gases given off by several varieties of rock, on heating. The subject has attracted some attention from previous experimenters. Thus Ansell and

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[*] 'Roy. Soc. Proc.,' vol. 59, p. 198, Jan., 1896.
[†] 'Comptes Rendus,' 1906, vol. 142, pp. 1155—1158.
[‡] 'Roy. Soc. Proc.,' vol. 73, 1904, p. 197.
[§] 'Roy. Soc. Proc.,' A, vol. 77, 1906, p. 482.
[||] *Loc. cit.*

Dewar,* and afterwards Tilden,† showed that the hydrogen evolved is probably not occluded in the rock, but has its origin in the reaction of metallic iron and water, which are both constituents. They also observed the evolution of carbonic acid, nitrogen, and methane.

I do not propose to give minute details of my experimental methods in this paper, since other experiments on the same lines are still in progress and may lead to improvements. The powdered rock was heated in an iron tube, and the evolved gases were extracted with a mercury pump in the ordinary way. After explosion with oxygen and absorption by caustic potash, the inert residue, consisting chiefly of nitrogen, was measured. The nitrogen was removed by sparking, and the residue introduced into a vacuum tube for spectroscopic examination. A further separation of the gases was made by means of Sir J. Dewar's method of absorption with cooled charcoal. In this way helium (with neon) could be isolated and pumped off. Argon was absorbed by the charcoal, and could be recovered on warming up.

The volumes of the inert gases were measured in the capillary tube of a gas pipette. The results for two normal rocks were as follows:—

Matopo Granite. Quantity taken, 850 grammes.

The inert residue consisted of—

Nitrogen	11 c.c.
Argon	0·14 c.c.
Helium	0·04 c.c.
Neon	traces

Syenite Rock, Mt. Sorrel, Leicestershire. Quantity taken, 900 grammes.

Inert residue—

Nitrogen	9 c.c.
Argon	0·026 c.c.
Helium	0·010 c.c.
Neon	traces

In both these cases the vacuum tube, after removal of argon, gave a brilliant yellow helium glow.

We may compare these analyses with the composition of the Bath gas, as a type of the gases evolved by mineral springs. The total volume of inert gas (mainly nitrogen) is taken as 100.

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* 'Roy. Soc. Proc.,' vol. 40, 1886, p. 549.
† 'Roy. Soc. Proc.,' vol. 60, 1896, p. 455.

Gas.	Argon.	Helium.	Neon.
	per cent.	per cent.	
Bath spring	1·5	0·12	traces
Matopo granite	1·27	0·36	traces
Syenite, Mt. Sorrel	0·29	0·11	traces

These figures make it fairly clear that there is a general resemblance between the gases of mineral springs and the gases of rocks, so far as nitrogen and the other inert constituents are concerned.

In addition to these constituents, rocks give off hydrogen, carbonic oxide, carbonic acid, and a little methane. The two former are probably secondary products, produced by chemical actions set up on heating. Carbonic acid is represented at the spring by the dissolved carbonates of the mineral water, while methane is present in the evolved gases. I think, therefore, that we may consider that the disintegration and partial solution of ordinary rocks by water at a high temperature accounts for the gaseous, as well as the solid, products delivered by springs such as those at Bath.

To collect enough gas from a rock for quantitative examination of the rare gases, repeated operations, requiring considerable labour, were necessary. Gases from the following rocks were merely examined qualitatively—augite syenite, from Laurvig, Norway; greenstone, St. Ives, Cornwall; olivine euchrite, Isle of Rum; red sandstone, East Lothian.

In each case nitrogen was present, and, on sparking down, the spectra of argon and helium were visible. Neon was not observed, but probably it would have been possible to detect it if more material had been worked up.

An exceptional case was found in commercial pumice-stone, which, I believe, comes from the Lipari Islands; 480 grammes of this gave 3·5 c.c. of nitrogen, which, on sparking down, yielded 0·049 c.c. of inert residue— 1·4 per cent. of the nitrogen. This inert residue showed the spectra of argon and neon, without helium; and after absorption in charcoal, neon alone remained. The presence of helium could not be detected with certainty.

With regard to the primary origin of the argon and neon contained in rocks, I have no theory to offer. It is natural, however, to associate the helium of rocks with the radium they contain. The relative quantities are quite in accordance with such a view, for the ratio is of the same order as in the strongly radio-active minerals. I hope to discuss this subject in detail in a future paper. I have found at least traces of helium in almost all of a considerable collection of ores and other minerals; but hitherto only one case has been found—in certain beryls—where there seems to be sufficient reason

to look for any other cause than traces of the radio-active elements to explain its presence. The evidence, so far obtained, is not favourable to the view that the ionising radiation from ordinary substances is accompanied by production of helium.

Assuming that helium in rocks has been generated *in situ* by radio-active change, it becomes of interest to enquire whether any connection can be traced between the quantity of helium and the time which has elapsed since solidification of the rock. With a view to answering this question, various modern lavas from Vesuvius of the eruptions of 1809, 1822, and 1906 were examined. Helium was detected in each case, accompanied, as usual, by argon. I had not enough material to determine the helium quantitatively, but it did not seem to be conspicuously less than usual. Probably the gases are unable to escape to more than a slight extent from a compact mass of melted lava.

The experiments recorded in this note are not regarded as in any way exhaustive. It has been thought well, however, to publish them, without waiting for the completion of the further enquiry which has been referred to, since they seem to throw light on a geological problem of independent interest.

Preliminary Note on a New Method of Measuring directly the Double-refraction in Strained Glass.

By L. N. G. FILON, M.A., D.Sc., Fellow and Lecturer of University College, London.

In general the methods employed for observing the double-refraction in strained glass depend on the use of crossed Nicols, and are similar in principle to those used for observing the colours of crystalline plates.

So far as the *difference* between the two indices of refraction is concerned, a method described by the author[*] allows of continuous observation of the double-refraction throughout the spectrum.

But with regard to the *absolute* change in the refractive index of either of the two polarised rays, into which light passing through the strained glass is broken up, the only method hitherto known for determining it is the one employed by Kerr[†] and by Pockels[‡]. This requires the use of homogeneous light, and of some form or other of interferometer. Very difficult and delicate adjustments are necessary, and, moreover, the method is not suited to observations extending continuously throughout the spectrum.

The following method is free from these objections, and depends upon an effect which appears interesting in itself.

Consider a horizontal beam of parallel homogeneous light incident normally upon the face AD of a rectangular glass slab of which ABCD represents the cross-section. The slab is under flexure in a vertical plane perpendicular to the direction of the incident light.
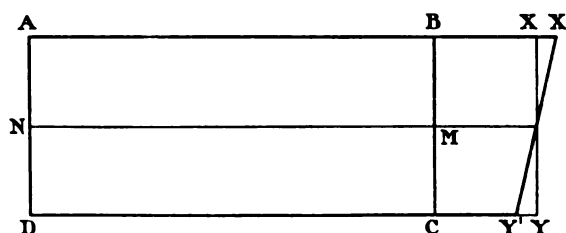
Let C_1 = stress-optical coefficient for the ray polarised in the plane of the cross-section, and for light of the given wave-length. Then if M = bending

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[*] 'Camb. Phil. Soc. Proceedings,' vol. 12, p. 55, *et seq.*, and 'Roy. Soc. Proc.,' A, vol. 79, pp. 200—202.

[†] 'Phil. Mag.,' October, 1888.

[‡] 'Ann. d. Phys.,' 1902.

moment, I = moment of inertia of the cross-section about the " neutral axis " MN, τ = thickness of slab, the retardation of a ray passing through at a distance y from the neutral axis is

$$(C_1 M\tau/I)\, y.$$

Thus the points at which the disturbance is in the same phase, instead of lying upon a line XY perpendicular to MN, lie upon a line X'Y' inclined to XY at an angle $\theta_1 = C_1 M\tau/I$.

Such a slab under flexure will therefore deflect the wave-front like a prism. It will do the same, only to a different extent, to the wave polarised in the perpendicular direction.

Thus if we analyse such a beam by means of a grating, the spectrum lines all appear doubled, the two components being oppositely polarised.

If ϕ be the angle of incidence on the grating, ψ the angle of diffraction of the wave of length λ, we have

$$\sin \phi - \sin \psi = n\lambda,$$

n being the number of lines per unit breadth of the grating. Whence

$$\frac{d\psi}{d\phi} = \frac{\cos \phi}{\cos \psi}.$$

Therefore the shifts of the spectrum line corresponding to wave-length λ, due to the effect of strain on the two oppositely polarised rays, are

$$\theta_1 \frac{\cos \phi}{\cos \psi}, \quad \theta_2 \frac{\cos \phi}{\cos \psi}.$$

By measuring these shifts, θ_1, θ_2 and therefore C_1, C_2 can be found. Hence the *absolute* changes in the two indices of refraction can be calculated, and this not only for one kind of light, but for as many kinds at once as there are lines visible in the spectrum under observation.

A correction has to be introduced on account of the fact that the glass slab, owing to lateral expansion under longitudinal pressure and contraction under tension, loses its rectangular shape and becomes a prism of very small angle. This causes an additional deflection of the wave-front after traversing the glass. This correction may be computed from the elastic constants of the glass, which have then to be determined, or it may be eliminated altogether by immersing the slab in a fluid whose refractive index is equal to that of the glass.

Actual experiment with a borosilicate glass, the total thickness traversed being 6 cm. and the difference of relative retardation per centimetre height about 10 wave-lengths for sodium light, showed the doubling most clearly. The grating used was a reflection grating of 14,000 lines to the inch, and

With the magnification employed the D lines were widely separated. The definition of the lines was not sensibly impaired by the thickness of glass traversed, and remained good when the load was applied.

The maximum load which could be applied with safety separated the two components of either D_1 or D_2 by an amount approximately equal to the original distance between the sodium lines, so that one component of D_1 was coincident with the other component of D_2.

On the Velocity of the Cathode Particles emitted by Various Metals under the Influence of Röntgen Rays, and its Bearing on the Theory of Atomic Disintegration.

By P. D. INNES, M.A., B.Sc., 1851 Exhibition Scholar of the University of Edinburgh; Trinity College, Cambridge.

The numerous theoretical and experimental investigations during the past few years of J. J. Thomson, Rutherford, Becquerel, and others on the radio-active substances have demonstrated conclusively that the only theory which can satisfactorily account for the phenomena observed is that of atomic disintegration, a process which is apparently going on in several, if not in all, of the elements. This process, however, seems to be entirely spontaneous, to depend only on the special substance under investigation, and to be outside the control of any external influence brought to bear upon it. Immense labour has been expended on experiments involving the utmost variation in the temperature and in the chemical and physical conditions of the elements, but all to no purpose so far as influencing the rate of atomic disintegration is concerned. As far as is known at present, no variation in the output of energy has been detected. There are, it is true, results by Curie and Danne,* and more recently by Makower,† which seem to show an effect of temperature on radium emanation. These results are not, however, confirmed by Bronson in his experiments on the same subject,‡ so that no definite conclusion can yet be reached on this point.

Obviously, it would be of immense interest and importance, not only from the scientific point of view, but also from the technical and commercial standpoint, if some method could be devised of stimulating or retarding at

* 'Comptes Rendus,' vol. 138, 1904, p. 748.
† 'Roy. Soc. Proc.,' vol. 77, 1906, p. 241.
‡ 'Amer. Jour. Sc.,' 1905, p. 60, and 'Phil. Mag.,' [6], vol. 11, 1906, p. 143.

will this output of atomic energy. That there is a great store of energy in the atom seems now beyond question, and if this reservoir could only become available, all our present conditions might be completely revolutionised. Naturally, the only mode of attacking this problem is by investigating what the nature of this atomic emission of energy is.

Now in the case of radium and the other properly so-called radio-active elements, in which the radiated energy is great, of different kinds, and continually being emitted, the question of investigating the factors influencing atomic disintegration is more complicated. There is, however, a simpler kind of disintegration, or, at least, of radiating power, and this, too, a kind which can be excited at will, and therefore it was natural to turn one's attention to it for a solution of the problem.

It was early discovered in the history of the Röntgen rays that, when they impinge on a metallic surface, they give rise to (1) a set of rays analogous to the original rays, but usually less penetrating, called the secondary rays; (2) negatively charged particles which can be deflected by an electric or magnetic field. The presence of these particles or cathode rays seems to indicate that here, too, there is a kind of atomic disintegration going on, somewhat similar to that which takes place in the radio-active elements, the cathode particles being corpuscles emitted or extracted from the atoms of the element. Such a conclusion, though very natural, is, however, not necessarily true, for it is quite possible to account for them in another way. The modern theories of electrical conduction assume that there is present in conductors a large number of free corpuscles, not intimately bound up in the atomic structure of the element, and it may be these electrons which are extracted or hurled out by the impulse of the impinging Röntgen rays. If such were the case, then there could be no question of tapping the energy of the atom, for there would be no atomic disintegration taking place.

There ought to be a possibility of discriminating between these two hypotheses. Granting, for the moment, that there is atomic disintegration, *i.e.*, that under the influence of the Röntgen rays a kind of explosion takes place in the atom, then the velocity of the corpuscle will be primarily that due to the energy of the explosion. We may regard the atom as receiving and storing up the energy of the primary rays. This will go on till at a certain stage the atom, now possessing the requisite energy or being in the proper condition, hurls out one or more of its corpuscles. Under these circumstances the original velocity of the ejected electron will be independent of the rate of reception of energy from the Röntgen rays, and will be that due to the explosion alone. The number of corpuscles given out

might conceivably, and indeed naturally would, vary, while the velocity might be different in different elements, as a result of difference in internal atomic structure, which would involve the reception of a different amount of energy to bring different atoms to the exploding stage, and also a different violence of explosion.

If, on the other hand, it was the free corpuscles which were hurled out by the impulse of the impinging rays, then a variation in their velocity of ejection with a varying intensity of the primary rays would naturally follow. It was from this standpoint that Professor J. J. Thomson proposed to me the experiment of which the following pages give an account.

Many experiments have already been performed investigating this secondary Röntgen radiation, notably by Curie and Sagnac,[*] Perrin,[†] and Dorn,[‡] while Sagnac has published a further paper.[§] The results of Curie and Sagnac and of Perrin show that these ejected cathode particles are of feeble penetrating power, being almost entirely absorbed in 1 mm. of air at atmospheric pressure, while Dorn has measured their velocities, and finds that they are not homogeneous. His values vary from $1 \cdot 8 \times 10^9$ cm./sec. to $8 \cdot 5 \times 10^9$ cm./sec., depending on the value of e/m adopted. These results, however, cannot be used to solve our problem, as Dorn took no pains to keep his rays of the same intensity or hardness except within very wide limits.

Experimental.

After due consideration it was decided that a photographic method offered several advantages over an electrical one, especially in that the results were permanent and could be referred to when desired as a check, while a magnetic field was used to deflect the cathode particles. Obviously, from Sagnac's results, the experiment had to be carried out *in vacuo*, and a specially good vacuum was required, otherwise the β particles would be scattered in their path and no clear lines would be obtained on the photographic plate.

The first method thought of was similar to that used by McKenzie in his determination of the velocity of the a rays from polonium,[||] *i.e.*, by placing a screen of zinc sulphide in front of the photographic plate and inside the vacuum ; this, on being struck by the rays, phosphoresced and affected the plate. A great advantage offered by this mode of experiment was that it

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* 'Jour. de Phys.,' [4], vol. 1, 1902, p. 13.
† 'Ann. de Chim. et Phys.,' [7], vol. 2, 1897, p. 496.
‡ 'Lorentz Jubilee Volume,' p. 595, 1900.
§ 'Ann. de Chim. et Phys.,' [7], vol. 22, p. 493, 1901.
|| 'Phil. Mag.,' [6], vol. 10, p. 538, 1905.

did not entail the renewing of the vacuum every time the apparatus had to be opened to insert a fresh plate. It was found, however, that the photographs so obtained were slightly fuzzy at the edges. Hence it was believed that more accurate measurements could be obtained if the rays were allowed to fall directly on the plate, even though the vacuum had to be renewed each exposure. The latter method was, therefore, immediately adopted in preference to that of McKenzie.

The Röntgen tubes used were fitted with an anticathode of stout platinum fixed on to a glass tube containing water, good contact being obtained by means of a wire sealed through this tube. Thus, a heavy current could be used with a minimum of risk to the tube. It may be mentioned that in an experiment such as this, where the rays require to be kept as constant in intensity and hardness as possible, the Röntgen bulbs are a constant source of trouble. The very heavy discharge which was required (as will be shown later), as well as the hardness of the rays which were frequently used, often broke them. This greatly hindered the progress of the experiment, one having sometimes to wait several weeks before the bulb was again available. To work the bulb, a 12-inch Apps induction coil was used.

It might be well to mention here the method of using the bulb which was adopted throughout the whole course of the experiments, in order to overcome the difficulty due to inconstancy of the rays. The bulb was allowed to work for one minute, then rest for two minutes or slightly longer, then one minute of work and so on. Such a method undoubtedly renders the work much slower; for example, it will be seen later that nearly four and a-half hours' exposure was required in some instances, so that the time required for the taking of one such photograph amounted to three days of continual work. The greater regularity and constancy of rays obtained were, however, considered well worth such an expenditure of time.

It might be convenient also to give at this stage the method used of testing the constancy and regularity of the Röntgen rays during the exposures. It is well known that if the rays impinge on a plate of lead, and the resulting ionisation of the air is driven back to the plate struck, a large leak is obtained. This ionisation is partly that due to the secondary Röntgen rays and partly to the cathode particles which we are investigating, and its total amount alters very much with a variation in the intensity or hardness of the tube. The apparatus consisted of a brass box (fig. 1) in the centre of one side of which was a circular hole 3·5 cm. in diameter. Inside the box and directly opposite this hole were placed a ring A of copper wire gauze and a circular lead plate B 2 mm. thick, each larger in diameter than the hole in

the side of the box by about 1 cm., the lead plate being surrounded by a guard ring. When the two were finally in position they were exactly parallel and 1 cm. apart. The gauze was insulated on an ebonite block D fixed to the bottom, and to it was attached a wire passing through a sulphur plug in one side of the box and leading to the accumulators. The lead plate was fastened at its centre to the end of a thin rod C, which passed out by the back of the
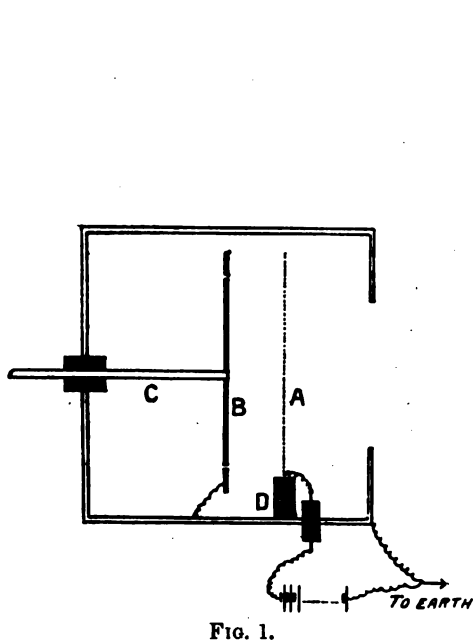
Fig. 1.
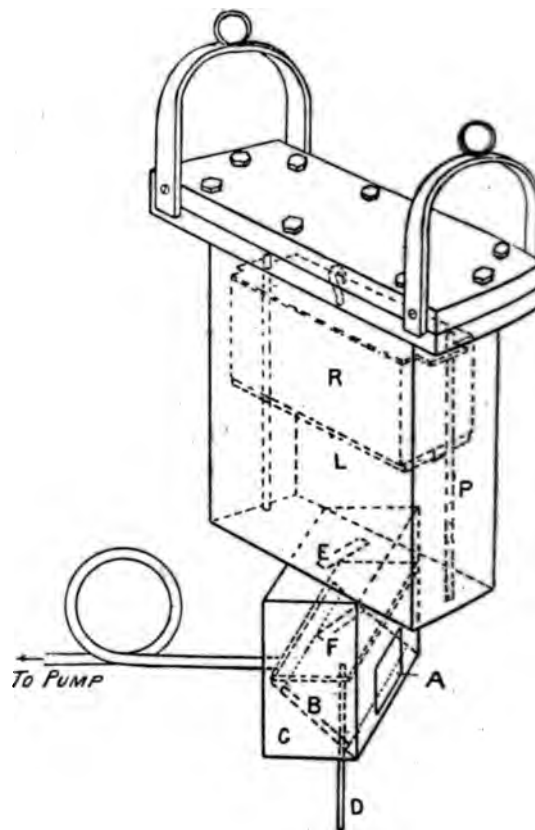
Fig. 2.

box, being again insulated with sulphur. This rod was connected up to a Wilson tilting electroscope, read by a microscope fitted with scale in the usual way. The box was placed immediately below the aluminium window of the apparatus, and tilted so that the X-rays fell directly through the gauze on to the lead plate. The measurements obtained by this apparatus were mainly intended to estimate the regularity of the Röntgen rays during exposures under exactly the same conditions, and not to compare different kinds of rays. It was found that the bulb could be kept so as to give a leak differing from previous measurements by only about 3 per cent.

An attempt was made roughly to measure the penetration of the rays by means of aluminium plates of different thicknesses and a standard plate of tin. The plates were placed in front of a platino-cyanide screen on which the rays were falling, and it was noted which aluminium plate gave the same absorption as the standard plate. The means finally adopted of estimating the hardness of the rays was the parallel spark gap, spherical brass electrodes of about 1·5 cm. diameter being used. The results are given with each plate.

Preliminary experiments with a simple form of apparatus to obtain the length of exposure necessary for a photograph showed that it was almost impossible, unless with very prolonged exposure, to get an impression on the photographic plate while the ordinary hammer-break of the induction coil was used, and as the Wehnelt Electrolytic Interrupter is not suited for giving constant rays, a turbine mercury interrupter was used throughout the experiments.

The apparatus found most suitable from preliminary experiment was wholly of brass 3 mm. thick, and was designed as follows (fig. 2). It consisted of an upper rectangular part 9 cm. broad by 2 cm. thick by 11 cm. high. To the bottom of this and in the centre was fixed, at an angle of 45°, a narrower portion of the same thickness 5·9 cm. long, but only 3·5 cm. broad. (The reason for its being turned at an angle of 45° to the top part will be apparent later from the description of the arrangement of the magnetic field.) In one side of this lower part, at a distance of about 0·5 cm. from the bottom, was cut the inlet A, 3 cm. broad by 1·5 cm. high, for the primary rays. A lead plate B, 3 cm. by 1·6 cm. by 2 mm., was fastened, insulated, on an ebonite block C, which again was fixed on a brass base, the ebonite being of such a size that it fitted exactly into the lower brass part of the apparatus, and so shaped that when it was sealed in by sealing wax, the lead reflecting plate was opposite the inlet A, and at an angle of 45° to the primary rays impinging horizontally. Through the brass base and the ebonite block passed a wire D, which was soldered to the lead reflector, and insulated by sealing wax, as it passed through the brass base. This wire permitted the metallic reflector being earthed or raised to any voltage thought convenient. I may here mention that this wire was kept earthed during the whole course of the experiments.

In two lead plates 2·1 mm. thick, and of such a size as to fit exactly into the lower part of the apparatus, were cut slits E and F, 10 mm. long and 1 mm. broad, at such an angle to the sides of the plates that when fitted into the apparatus the slits were exactly parallel to each other, and vertically beneath the centre of the broad upper part, their long edges being perpendicular to the long edges of the upper part of the apparatus, and, a will be

seen later, parallel to the lines of force in the magnetic field.   The slits were fixed during the experiments with the lead reflector, at a distance of 3·15 cm. between their middle points, the lower one being 0·2 cm. above the inlet A. The inlet was covered with aluminium foil 0·1 mm. thick, strengthened by a mesh of aluminium 0·4 mm. thick placed under it, an air-tight joint being obtained by means of sealing-wax.

The apparatus was connected to a Töpler pump and McLeod gauge by a tube bent to exclude the light.
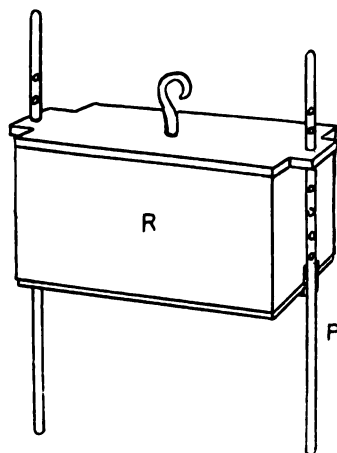
FIG. 3.
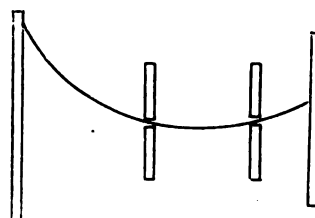
FIG. 4.

Within the upper part of the apparatus was inserted the photographic plate-holder R (fig. 3).   The holder was of brass, and fitted exactly, so as to slide smoothly up and down.   It could be fixed at any required distance above the slits by means of a thin brass rod P passing through a hole in the top of the holder.   This rod had small holes bored in it at intervals of 1 cm., so that a thin brass pin could be inserted in any hole, and on this pin the top of the holder rested.   Thus the plate could be fixed at any required distance above the slit.   The strip L of photographic plate inserted was of ¼-plate length and 1·9 cm. broad.   This size was chosen to avoid exerting pressure on the plates while cutting them into very small parts, it having been found from previous experience that such pressure tended to fog sensitive plates considerably.

Two thick smoothly planed brass plates 1 cm. thick were taken, and one of them soldered to the top of the apparatus.   Holes were bored in these plates and by means of nuts (all of brass, as they were to be in a magnetic field) they could be pressed firmly together.   Lead wires were drawn, and one was placed inside the nuts between the brass plates, just like a washer.   When

the nuts were screwed up, it was found that a high vacuum could be readily obtained and maintained for a considerable time.

A great many different kinds of photographic plates were tried :—Ilford Ordinary, Ilford Monarch, Cadett Ordinary, Cadett Lightning, Cadett Spectrum, Imperial Ordinary, Seed Orthochromatic, Lumière Σ, and Wratten-Wainwright spectrum plates. These brands of plates range from comparatively slow to very fast, and it is of interest to note that those plates which are most sensitive to ordinary light are by no means in the same category when it is a question of photographing β particles. Thus the Wratten-Wainwright plates, which are extremely sensitive, giving the potassium lines quite easily, were quite unsuitable for this work. The most suitable here were Cadett Spectrum, Lumière Σ, and Seed Orthochromatic, and it is the last named plates that have been mainly used.

Arrangement of the Magnetic Field.

At first a horse-shoe electro-magnet was used. This was soon discarded in favour of a magnetic field induced by two coils used in the manner of a Helmholtz galvanometer. With such an arrangement, the field is uniform almost up to the boundary of the coils,* and can be most readily calculated. In these circumstances, too, the particles were, during the whole of their path, under the influence of a uniform magnetic field, and consequently moved in a circle, thus immensely simplifying the process of calculating the velocity. The coils were most carefully wound on mahogany grooves, there being in each coil 17 turns and 19 layers—*i.e.*, 323 turns in all. Their circumference was measured by a steel tape after each successive layer, and the mean radius calculated from this. Its value was 24·233 cm. The principal galvanometer constant at the centre to unit current absolute was therefore 83·7376. These calculated constants were checked by comparing the magnetometric deflection obtained with these coils with the deflection due to another standard coil, the circumstances being similar. The agreement was found to be very satisfactory. The coils were placed parallel to the longer edges of the upper part of the apparatus, and so perpendicular to the slits.

The induction coil was placed at such a distance that its field was practically negligible, while its orientation with reference to the apparatus was such that any field due to it was perpendicular to the magnetic field of the coils, and had, therefore, no effect on the deviation of the cathode particles.

The whole arrangement was placed so that the angle between the earth's horizontal magnetic field and that of the coils was 85°. As the earth's

* See Maxwell's ' Electricity.'

horizontal field has only a value of about 0·180, the effect of this resolved along the direction of the magnetic field will be negligible.

The choice of Helmholtz coils had this further advantage that the Röntgen tube could be placed inside these, and so brought closer to the inlet A, thus shortening the length of exposure. If, however, the tube is to be placed inside the magnetic coils, it has obviously to be turned so that the path of the discharge inside it is parallel to the lines of magnetic force, otherwise the cathode discharge would be so much deflected by the field that it would not strike against the anticathode. Such was actually found to be the case during the experiment. It was for this reason that the lower portion of the apparatus was turned at an angle of 45° to the upper part, thus allowing the bulb to lie along the lines of force, and permitting the X rays to enter at A.

When the field is turned on, the cathode particles emitted from the reflector move in a circle. They come off the plate in all directions, but only those which come off at such an angle that their circular path due to the field can pass through the two slits will be able to reach the photographic plate (fig. 4). If, as is nearly the case, all directions are the same, in regard to the number of particles emitted, we shall get as many capable by a circular path of reaching the photographic plate as we should have if we took a pencil of particles proceeding in any one direction (*e.g.*, vertically), and then deviated them. If v is the velocity of the particles, and H the magnetic field, then

$$\frac{mv^2}{\rho} = \mathrm{H}ev, \quad \text{therefore} \quad v = \mathrm{H}\rho\,\frac{e}{m},$$

where m and e are respectively the mass and charge of the electron, ρ being the radius of the circle traced out by the path.

Since, as previously stated, these circular paths pass through the two slits, we have two points whose co-ordinates are given. The third point on the path is given by the photograph and, therefore, by measuring the deflection we can fix the circle completely. We can, of course, at once calculate ρ, and we know H. Throughout the work I have taken e/m to be invariable, as I assume the electrons which come under notice here to be similar to the ones usually obtained, an assumption which, as it seems to me, is quite reasonable from the results of many experiments on this quantity. The value taken for e/m is $1·7 \times 10^7$.

Results.

The results obtained for the various metals with the different kinds of Röntgen rays are given in the following tables. It was found that the photographs were not dense enough to be measurable by a microscope, so another

method was adopted. They were projected by an arc lamp on to a sheet, along with a Zeiss 10 mm. scale. One observer sketched in the image to the dictation of another standing farther away; then the process was repeated, the observers being interchanged, thus eliminating the error due to the person. The magnification was usually about 22 times. Each plate was then measured with a pair of very fine-pointed dividers, and the results got by the two methods compared. The agreement was found to be very satisfactory.

The pressure was in all the experiments less than 0·003 mm. of mercury as measured by the McLeod gauge. The distance between the middle points of the slits was 3·15 cm., while the photographic plate was 4·049 cm. above the upper slit. The current in magnetic coils was 1·5 ampères in every case.

Table I.—Lead.

No. of plate.	Parallel spark gap.	Current in primary.	Distance from Al inlet.	Exposure in minutes.	Deviation in mm.		Velocity ÷ 10⁹.	
					Fastest.	Slowest.	Fastest.	Slowest.
	cm.	amp.	cm.				cm./sec.	cm./sec.
a	5·1	6·0	6·0	31	3·98	4·95	7·8	6·3
b	5·1	6·0	6·4	31	4·10	4·90	7·6	6·4
c	5·5	6·5	19·3	46	4·10	4·98	7·6	6·3
d	5·5	6·4	50·0	130	4·04	5·01	7·8	6·2
e	16·0	6·7	6·5	46	3·76	4·88	8·3	6·4

Prints of the photographs of the above plates are here appended (p. 452). I should remark that, as they have been intensified with uranium, and the film is somewhat broken and ragged, they do not print well. The cutting of the plates, and the scratching due to their being put into the holder, does, of course, tend to injure the film. The negatives themselves are much more easy to measure. All the plates mentioned above are given here in order to show where they are alike and where they differ.

Plates a and b are types of those taken under exactly similar circumstances; c and d are examples of those obtained with different intensity of bulb, got by varying the distance of the bulb. It is to be noted here that the bulb is slightly harder, the spark gap being 5·5 cm. instead of 5·1 cm.; e is one of the photographs got with much harder rays.

An examination of the results of a, b, c, and d shows that the varying of the distance of the Röntgen bulb from the reflector causes practically no change in the velocity of the fastest cathode particles emitted, their mean velocity being 7·67 × 10⁹ and greatest difference from this less than 2 per cent

Besides varying the distance of the bulb, means were taken to vary the current passing through it by a variation of the current in the primary of the induction coil; this varied from 3 ampères to 9 ampères. No difference of velocity was, however, observed. Then the rate of the mercury interrupter was varied, thus altering the number of interruptions of the current in unit time, but here also no change was observable. We therefore conclude that this fastest velocity is quite independent of the intensity of the rays. (It has not been thought necessary to give these photographs, as they are similar to the ones already given.)

a

b

c

d

e
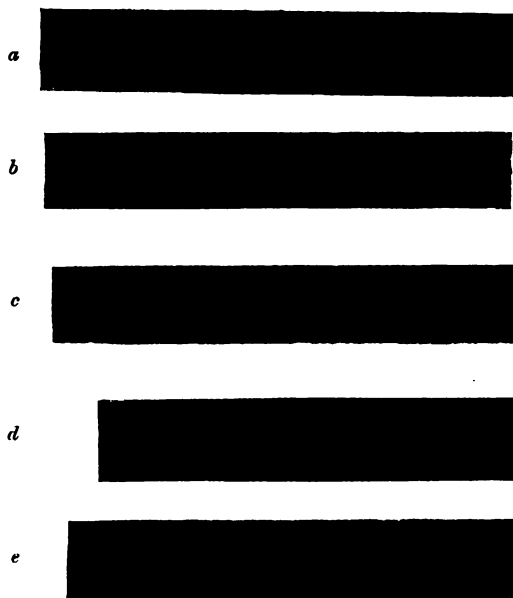
When, however, we examine plate *c*, an example of the hard ray photographs, we find a fairly large difference in the velocity of the fastest particles, amounting to about 7 per cent. This difference is quite beyond the limit of experimental error, as is shown by the agreement of the other plates. This result is typical of all the plates taken with the hard rays.

It is interesting to compare the duration of exposure necessary in the different cases. The farther away the bulb is, the longer is the exposure required, thus showing that the intensity does influence the number of particles given off. An increase in the hardness of the tube has the same effect on the number emitted as a decrease of intensity.

I may mention that only the minimum number of confirmatory photographs were taken with very hard rays in the case of lead and also of all the other

metals used, as it was in this condition that the tube most frequently "sparked through" and became useless.

When we turn our attention to the velocities of the slowest particles emitted, we find that there is not such close agreement in the results obtained. This was owing to the line being more indistinct than was the case with that due to the fastest rays, doubtless because fewer of the slow ones are emitted. This is what we should expect, if we take the view (which seems the only natural one), that the cause of the reduced velocity of these particles is that they come from a lower layer in the metal, and hence are retarded in their progress to the surface. Besides being retarded, they would also get scattered, so that only a few of those emitted originally would emerge at the surface.

It is interesting to note, however, that the results of the various plates, though not so consistent as those of the fastest particles, are quite within the limit of error made in the measurement of the most deviated edge of the line in any one plate, and we can therefore say that, so far as experiment goes, it shows them to be the same. It is quite evident from the negatives that the line does not gradually diminish in intensity down to zero, and we therefore conclude that there does seem to be a definite minimum velocity which the particles must possess if they are to emerge. Particles with a velocity less than this minimum will get caught and remain inside the metal.

Table II.—Silver.

No. of plate.	Parallel spark gap.	Current through primary.	Distance of bulb from Al inlet.	Exposure in minutes.	Deviation in mm.		Velocity + 10⁹.	
					Fastest.	Slowest.	Fastest.	Slowest.
	cm.	amp.	cm.				cm./sec.	cm./sec.
a	3·9	7·3	6·0	145	4·37	5·2	7·2	6·0
b	4·1	7·6	20·0	200	4·28	5·21	7·3	6·0
c	19·0	9·2	6·1	252	3·9	5·13	8·0	6·1

a

b

c

The details have been given of only a few of the photographs taken with this metal, as to give more would merely recount many of the remarks made regarding those with lead. The velocity, as may be seen from the typical plates *a* and *b*, was again independent of the intensity of the rays or the current passing through the tube and varied only with the hardness, as witness the example plate *c*. The plates taken under similar circumstances again agreed within about 2 per cent., as also did those obtained with different intensities, while the hard rays gave a velocity of about 10 per cent. greater for the fastest particles. This is more than in the case of lead, but it must be remarked that the bulb was harder with silver than with lead.

One very interesting point is that the velocities here got for the fastest particles are lower both with soft and hard rays than they were with lead, and that the differences between those got with soft rays and those got with hard rays are much the same if we take into account the fact of the tube being slightly harder for plate *c* of silver than for plate *e* of lead.

The velocities of the slowest particles are, however, of very nearly the same magnitude as those got with lead, at least there is no such marked variation, and the same remarks apply here as did to the slowest lead particles. The long time of exposure necessary with silver is somewhat surprising in view of the fact that its atomic weight is more than half that of lead. Here, too, it varies with the intensity and hardness of the rays.

Zinc.

Photographs were taken with very soft rays impinging on zinc. The following is given as an example of the results obtained :—

Table III.

No. of plate.	Parallel spark gap.	Current through primary.	Distance of bulb from Al inlet.	Exposure in minutes.	Deviation in mm.		Velocity ÷ 10⁹.	
					Fastest.	Slowest.	Fastest.	Slowest.
a	cm. 3·9	amp. 6·8	cm. 6	230	4·87	5·2	cm./sec. 6·4	cm./sec. 6·0

The print given by this is the accompanying one, and is seen to be rather indistinct, despite the long exposure. The negative is of course better.

Other photographs with the same hardness and intensity confirmed this result, the differences between the results being of a similar magnitude to those existing for lead and silver. The velocity is here also independent of the intensity. It is interesting to note, however, that the velocity of the fastest particles emitted from zinc have a velocity much lower than that obtained for lead or silver, the difference being about 16 per cent. if we compare it with the velocity of the lead particles when the tube was in a similar condition. The atomic weight of zinc is, of course, 65·5.

The bulb having been hardened up, attempts were made to get a photograph, but when an exposure of several hours gave no result it was decided to pass on to other metals, especially as fears were entertained regarding the safety of the tube when running so long in a hard condition.

The slowest particles have a velocity almost the same as those of silver.

Table IV.—Platinum.

No. of plate.	Parallel spark gap.	Current through primary.	Distance from Al inlet.	Exposure in minutes.	Deviation in mm.		Velocity + 10⁹.	
					Fastest.	Slowest.	Fastest.	Slowest.
	cm.	amp.	cm.				cm./sec.	cm./sec.
a	3·2	4·8	6·3	40	4·2	5·1	7·4	6·1
b	3·6	5·0	20·0	56	4·1	5·05	7·5	6·1
c	14·0	4·0	6·1	55	3·85	4·7	8·0	6·5

The distance between the slits was in this case 3·05 cm., the magnetic field being kept as before. The prints from these negatives are the following ones. A curious third line appears in one of them, but as this does not

a

b

c

come out in any of the others no·explanation can be given of its presence. The results have of course been confirmed by other photographs, those given

here being printed as examples of what was obtained.   The print of plate *c* apparently shows a deflected line much narrower than that occurring in the other plates.   Although this is to some extent the case, as can be seen from the results calculated by measurement of the negative, yet the print seems greatly to exaggerate the difference.

Here again it is apparent that the velocity of the fastest particles is independent of the intensity, but does increase with increasing hardness of the tube.   The velocity is less than that of the lead particles, but greater than that of silver.   The difference between the results for lead and those for platinum is small, but even if the velocity does depend on the atomic weight, we should not expect a great difference, their atomic weights being so near to one another.   Lead has an atomic weight of 207, while that of platinum is 195.

As regards the slowest particles, an interesting point is that they seem to have much the same velocity as resulted from the other metals, if we remember the greater inaccuracy which is possible in measuring their deflection, due, as explained before, to the somewhat indistinct nature of this edge of the line.

Table V.—Gold.

No. of plate.	Parallel spark gap.	Current through primary.	Distance of tube from Al inlet.	Exposure in minutes.	Deviation in mm.		Velocity ÷ 10⁹.	
					Fastest.	Slowest.	Fastest.	Slowest.
	cm.	amp.	cm.				cm./sec.	cm./sec.
a	3·4	5·0	5·5	25	4·1	5·05	7·5	6·1
b	3·6	4·8	18·0	50	4·05	5·0	7·6	6·2
c	15·0	6·0	6·0	32	3·8	4·97	8·1	6·2

For this metal the distance between the slits was 3·025 cm. with the same magnetic field as before.   The prints are the following—

a

b

c
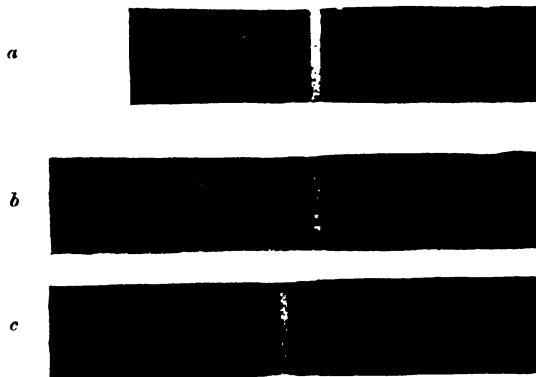
It is apparent from plates *a* and *b* that the velocity of the particles is independent of the intensity of the rays, while *c* shows how the velocity varies with increasing hardness. The plates were confirmed in each case by others taken under similar circumstances.

It is at once apparent that the velocities obtained with gold are practically identical with those in the case of platinum, which is what we should expect if it depends on the atomic weight. The same remarks apply to the slowest velocities as did formerly to those of platinum.

Discussion of the Results and Conclusions.

It will be of advantage to compare the velocities obtained with those got by Dorn, in his earlier work. He found velocities varying from $5\cdot3 \times 10^9$ to $8\cdot5 \times 10^9$, on the assumption that e/m had a value of $1\cdot865 \times 10^7$. As the value of e/m here used is $1\cdot7 \times 10^7$, we must reduce his results by practically 9 per cent. This would give values of about $4\cdot9 \times 10^9$ to $7\cdot8 \times 10^9$. Now it is to be remembered that Dorn did not trouble himself very much about keeping the hardness of his Röntgen tube exactly the same. He himself says that "generally rays corresponding to a parallel spark gap of 10 cm. to 20 cm. were used, and when the tube became harder than this the experiment was stopped while the tube was softened." It will, therefore, be admitted that, since the velocity varies with the hardness, the agreement of the present results with those of Dorn is satisfactory.

A few weeks ago, just as this work was nearing completion, a paper was published by Bestelmeyer.[*] He only used one metal, viz., platinum, in his experiments, and though he says that the velocity varied with the hardness of the tube but not with the intensity, yet he does not mention what hardness of tube he used in the various exposures. His results, taking e/m to be $1\cdot7 \times 10^7$, which is the same value as I have assumed, vary from $5\cdot9 \times 10^9$ to $9\cdot6 \times 10^9$; thus they are higher, while those of Dorn were lower, than the results given by me for the fastest particles emitted. Bestelmeyer's results for the slowest particles are practically identical with my own.

The most remarkable fact which arises out of the results given in this paper is the complete absence of any effect of the intensity of the Röntgen rays on the velocity of the cathode particles emitted. As we have seen, we may vary the current passing through the tube, or the number of interruptions per unit of time of the current in the primary of the induction coil, and no change is apparent in the velocity. Again, the tube may be taken farther away, but still we get no change in the velocity. Now if the

[*] 'Annalen der Physik.'

cathode particles are ejected by the energy of the impinging Röntgen rays, it is at once evident that a change is to be expected in the velocity of the emitted β particles.

Let us take as the simplest case that of an electron free to move and not held in position by other forces. (The more complicated case of an electron maintained in equilibrium by attractive and repulsive forces can be treated by supposing* that the effective mass of the electron is increased.) If X is the force in the pulse, and δ the breadth of the pulse, while e and m are respectively the change and the mass of the electron, then Xe is the impulse acting on the electron, and we have

$$Xet = mv,$$

where $t = \delta/V$ (V = velocity of light) is the time taken by the electro-magnetic pulse to pass over the electron and v is the resulting electronic velocity.

Now it is natural to assume that the effective mass m of the electron will not vary for atoms of the same element, while that the charge e is invariable is proved by a large number of experiments. If, however, we alter the position of the tube, with reference to the metallic reflector emitting the β rays, keeping its hardness and intensity the same, then the breadth of the pulse will remain as before, but the force X will vary inversely as the square of the distance of the tube from the metal. It follows, therefore, that the velocity acquired by the electron in this latter case cannot possibly be the same as in the first instance.

As was pointed out in the introduction to this paper, a suggestion has been put forward that the β particles got here are the free electrons occurring in the metal, and that they have been ejected by the electro-magnetic energy of the Röntgen rays. If this were so, we should necessarily expect, as stated already, a dependence of the velocity of ejection on the velocity of the primary rays, and as this is not the case, we have strong evidence for the view that the expulsion of these β particles is due to disintegration of the atom, and that the velocity acquired by the electron is that imparted by the energy of this disintegration.

This view receives additional confirmation if we take into account the values obtained for the velocities, *i.e.*, a velocity greater than 10^9 cm. per second was obtained in each case. Now, if this velocity were derived entirely from the energy of the incident rays, it is easy to show by calcula-tion that it could not possibly attain to this value.† For if X is the force

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* See J. J. Thomson's 'Conduction through Gases,' 2nd edition, p. 376.
† See J. J. Thomson's 'Conduction through Gases,' p. 320.

in the pulse, and $t = \delta/V$ is the time taken by the pulse to pass over the electron, then

$$v = 10^9 = X \frac{e}{m} t,$$

and putting

$$e/m = 1\cdot7 \times 10^7,$$

$$Xt = 60 \text{ approximately}.$$

Now the energy of the incident pulse per unit area is

$$\frac{1}{4\pi} \frac{X^2\delta}{v^2} = \frac{1}{4\pi} \frac{X^2t^2}{\delta} = \frac{3600}{4\pi\delta}.$$

Wien[*] has shown that δ for the rays examined by him had a value of about 10^{-8} cm., but even if we go much further, and assume $\delta = 10^{-5}$, which must be an upper limit, we should still get the energy per unit area of the incident pulse to be almost a calorie. This value we at once perceive to be far too great for acceptance.

It is instructive to note that the velocity of the fastest particles omitted varies from metal to metal, decreasing with decreasing atomic weight. This fact is an additional argument for the disintegration theory, showing, as it does, that there is a definite energy of disintegrating possessed by the atoms of an element.

Bumstead has published a paper,[†] the results of which seem to be very strongly in accord with the disintegration theory supported above. He finds that the impinging Röntgen rays, when equally absorbed by different metals, give rise to different heating effects. This is quite in agreement with the results given in this paper, for it is not to be expected that the explosion will be equally violent in all elements. If we assume that the velocity of the fastest emitted particles is a measure of the relative energy of disintegration in each metal, then, from the variation of this velocity mentioned above, we should expect to have different energies liberated. Take for comparison the metals lead and zinc, which are the two used by Bumstead. The velocity of the fastest lead particles is $7\cdot8 \times 10^9$ cm. per second, and that of the fastest zinc particles $6\cdot5 \times 10^9$ cm. per second, if the conditions of the primary rays are nearly the same. On the assumption mentioned above, regarding the velocity and energy of explosion, we should say that the energy liberated in lead would be about $1\cdot2$ times that liberated in zinc. Bumstead found that the energy liberated in lead was $1\cdot9$ times that liberated in zinc.

It is satisfactory to find that, from my results, a greater amount of heat

* 'Ann. der Physik,' vol. 18, 1905, p. 991.

† 'Phil. Mag.,' [6], vol. 11, 1906, p. 292.

might be expected to be obtained in lead than in zinc, a result obtained before by Bumstead. This suggests that there is at least some truth in the assumption mentioned above; it is only a suggestion, however, as so many other factors come in. Thus the number of particles given off, *i.e.*, the number of explosions taking place, would naturally have a great influence, and this would, if we take into account the duration of exposure necessary for photographing, greatly increase the relative energy generated in lead. Again, the number of particles coming from a layer too low to be emitted, whose kinetic energy is completely absorbed in the body of the metal, and which never emerge at the surface, is a factor not to be neglected; this would naturally be greatly dependent on the number of atoms " exploded " at the various depths by the Röntgen rays, as they penetrated the two metals, a number not necessarily varying directly as the energy of primary rays absorbed in each successive layer (for, as will be discussed later, every atom of an element does not require the same amount of energy to enable it to disintegrate). Hence it is not possible to get, by simple calculation, the relative amounts of the total energy liberated in the above metals, even if the assumption made earlier were quite true, until further investigation reveals more concerning the influencing factors mentioned above. It is, however, interesting to find that the results are at least qualitatively in agreement.

Barkla[*] has shown that the penetrating power of the secondary Röntgen rays is independent of the intensity of the primary rays, and this result certainly helps to confirm the theory of atomic disintegration. He remarks that the fact discovered by him, that the secondary rays were never more penetrating than the primary rays, is strongly against any idea that atoms are " exploded," implying that if this were so, a very penetrating radiation would be produced. This is not necessarily the case, for the corpuscles may not, in fact probably do not, derive all their velocity from the energy of the disintegration, and the greater and perhaps more penetrating part of the secondary radiation is that due to the acceleration of the corpuscles in the atom. If this were not so, we should expect that the greater the velocity possessed by these corpuscles, the more penetrating would be the secondary radiation. This is, however, by no means the case, for, as we have seen, this velocity certainly decreases (though comparatively slowly) with decreasing atomic weight, whereas Barkla finds that the elements of lower atomic weight (*e.g.*, aluminium) give the most penetrating secondary radiation.

The fact that the velocity of the electron emitted increases with the hardness of the rays does not militate against the disintegration theory.

* 'Phil. Mag.,' [6], vol. 11, 1906, p. 812.

Professor Thomson has, in his well-known papers on the structure of the atom, shown that a great many of the known properties of matter and the resulting phenomena can be explained by assuming an atom built up of corpuscles arranged in rings in a sphere of positive electricity. Now, the difference between hard and soft Röntgen rays being that of different electric force and breadth of pulse, it may be the case that the hard rays are able to displace one or more of the corpuscles situated in an inner ring. If this were so, then the repulsive forces of the atom might have longer to act on the corpuscle and so eject it at a greater rate.

The disintegration theory gives an explanation, too, of the decrease in the number given off with decreasing intensity of primary rays, as, the energy imparted by each pulse being smaller, more pulses must pass over an atom before it reaches the proper stage. A similar explanation applies to the decreased number emitted with hard rays which are less absorbed.

The atoms of an element will, of course, not be all in the same state. Some will be near the exploding stage and others will be a long way from it, so that we get some idea of the reason why all atoms are not ionised when struck by Röntgen rays. Again, the number of atoms in the various elements in the different stages of disintegration is not necessarily the same, so different times of exposure are required.

It will be noticed that only the metals of large atomic weight have been investigated and, from the results with zinc, it is apparent that a photographic method cannot be used with success in the case of the metals of low atomic weight. Since Barkla finds a disappearance of scattering of the Röntgen rays at a certain stage, it seems to be of interest to go on to the examination of these metals of low atomic weight. An electrical method has been devised which it is hoped will effect the investigation of these velocities.

Summary of Results and Conclusions.

1. The velocity of the electrons emitted by lead, silver, zinc, platinum, and gold under the influence of Röntgen rays has been measured, both for soft and hard rays.

2. The values found are as follows, the accuracy being within about 3 per cent. :—

	Soft Rays.	Hard Rays.
Lead	6·3 to 7·6 × 10^9	6·3 to 8·3 × 10^9
Silver	6·0 to 7·2 × 10^9	6·1 to 8·0 × 10^9
Zinc	6·0 to 6·4 × 10^9	
Platinum	6·1 to 7·5 × 10^9	6·4 to 8·1 × 10^9
Gold	6·1 to 7·5 × 10^9	6·2 to 8·1 × 10^9

3. The velocity of the fastest electrons emitted from each metal is completely independent of the intensity of the primary rays, but increases with the hardness of the tube.

4. The velocity decreases with the atomic weight, the difference between the speed of the fastest electron with hard rays and that with soft rays being practically the same for the various metals, if the variation in hardness of the rays is the same.

5. A minimum velocity is necessary to enable the electron to emerge, and the minimum velocity is nearly the same in the different metals.

6. The number of electrons given off decreases with decreasing intensity of the rays, as well as with increasing hardness.

7. The number emitted also decreases with decreasing atomic weight and density.

8. The conclusion is drawn from calculation and discussion of other theories, that the most probable theory is that of atomic disintegration. It is shown that the velocity of the emitted electron is too great to be that acquired under the influence of the electric force in the X ray pulse. The other theory of ejection is discussed and objections to it pointed out. A possible explanation is given of the increase of the velocity with increasing hardness of the rays, and this fact is shown not to be inconsistent with the disintegration theory.

It is a pleasure to me, in conclusion, to acknowledge the keen interest and ever helpful encouragement of Professor J. J. Thomson during the whole course of the experiments, and I desire to tender him my most sincere thanks.

The Hard and Soft States in Ductile Metals.

By G. T. BEILBY, F.R.S.

(Received June 20,—Read June 27, 1907.)

The Micro-structure of Hard-drawn Gold Wires.

In connection with the previous research* attempts were made to break down the crystalline structure of the metal as completely as possible by wire drawing. On etching the surface of wires prepared in this way the structure disclosed appeared to be finely granular, no traces of crystalline grains or of patches of uniform orientation being visible. After the publication of the former paper the wires which had been then used were subjected to a more searching examination. Specimens were ground so as to expose longitudinal sections at various depths and these were etched till the true understructure was disclosed. At low magnifications the structure appeared to consist of parallel strands or fibres which became thinner and either pinched out or drew closer together at the point of fracture. The general character of this structure is shown on fig. 1, which is a diagrammatic sketch of the fractured end of a hard-drawn gold wire.
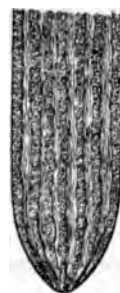
Fig. 1.

For the proper resolution of the intimate structure of these strands or

Fig. 2.—Magnification × 700.   Fig. 3.—Magnification × 700.

* 'Roy. Soc. Proc.,' A, vol. 76, p. 462.

fibres, a lens of fairly high N.A. is necessary, and in the photomicrographs, figs. 2 and 3, a 4-mm. objective of 0·95 N.A. was found most suitable.

On fig. 2 the etching has not penetrated very deeply, and portions of the surface are still covered by the remains of the disturbed layer which had been produced by the grinding and polishing; but on the lighter parts of the photograph the internal structure is plainly disclosed, and it is seen that the strands or fibres are composed of grains which have been drawn out and pinched into long torpedo-like forms. Fig. 4 is a diagrammatic sketch of this type of structure.

Fig. 3 shows the effect of etching away still more of the matrix of amorphous metal, and with it the smaller fragments of crystalline grains. In photographing this specimen, as the irregularity of the surface made it impossible to get more than a small part in perfect focus at one time, that adjustment of focus was chosen which gave the best general idea of the arrangement of the comparatively large masses which have survived the severe treatment of wire drawing. The material which has been removed from between these ridges is the more soluble, but also the more mechanically stable, amorphous metal which has acted as a rigid matrix to the deformed grains which are enclosed within it. During the successive stages of stretching it seems probable that within any given portion of the wire the *rôles* of protector and protected may be taken in turn by the substance of adjoining grains. A breakdown of structure occurring in certain grains or lamellæ will result in the momentary production of a relatively large quantity of the mobile phase at the rubbing surfaces, so that for this moment the line of least resistance will be through these grains which will, therefore, take the chief part in the adjustment of strain. But the momentary mobility having given place to the rigidity of the hardened state, this will become the line of greatest resistance, and the stress will now fall on the adjoining grains or lamellæ, which will in their turn break down and flow and in so doing will play their part in the adjustment of strains. Under an augmenting stress, these alternations will naturally continue till the rigidity of the matrix as a whole becomes so great that it will break rather than yield. The present observations show that this stage is reached while there are still comparatively large masses of crystalline substance which have been concreted into rigidity by the flow which has occurred at surfaces within the mass. These masses do not consist of uniformly

FIG. 4.

oriented lamellæ, but are a conglomerate made up of deformed lamellæ cemented together by flowed metal (fig. 3). These results confirm the conclusions of the earlier research, that the mechanical stability of the amorphous state gives even to the thinnest films an extraordinary power to protect from further destruction the masses of crystalline phase which they enclose.

The persistence of the crystalline phase under the most severe mechanical treatment is well illustrated in the case of gold leaf. In my earlier observations on thin metal films I adopted Faraday's conclusion, that when a gold leaf is floated on a solution of potassium cyanide, the metal is uniformly reduced in thickness by the action of the solvent. Subsequent observations have satisfied me that this is not the case. The cyanide does not proceed by dissolving away the surface uniformly, but it first attacks the amorphous metal, removing it and penetrating right through the substance of the leaf, so that the attenuated film which remains is a skeleton built up of the minute units of the crystalline phase which have survived the severe ordeal of beating. These units are, of course, much too minute to exhibit any crystalline micro-structure, so that but for their difference in solubility they would have escaped detection. A gold leaf may be compared to a light gauzy fabric which has been stiffened by a coating of gum or starch. As the removal of the gum by solution will restore the fabric to its original openness and pliability, so the removal of the flowed amorphous metal by solution leaves the gold leaf with an open spongy texture. A leaf which has been treated in this way absorbs water like a sponge, and in the wet condition appears to have a thickness much greater than that of the original leaf. When spread on a glass plate and dried it becomes less transparent, owing to the replacement of the water by air, and at the same time the appearance of thickness vanishes. The failure of the drastic operation of gold beating to convert the whole of the metal of so thin a film into the amorphous phase suggests that the complete conversion cannot be effected by any purely mechanical process. Observations on the thickness of the surface layer developed by polishing show that the apparently homogeneous layer to which the liquid-like surface is due is not many molecules in thickness, even though the mechanical disturbance penetrates to a much greater depth. As this subject will be fully discussed in another communication, it is not necessary to refer to it further in the present connection.

For the metallurgist and the engineer these observations are of importance, in so far as they show that the hardness which is conferred on ductile metals by any form of cold working is due to the development of a structure in which the distorted remains of the crystalline units are cemented together by a portion

2 i 2

of the metal itself which has momentarily flowed around them, and has then congealed into a harder and more resistant form of the metal. Among alloys, metallurgists are familiar with many cases in which rigidity is conferred by the concreting action of one of the constituents separated during crystallisation, but in the pure metals hardening does not result from the building up of a new crystalline structure, but from the breaking down and flow of the already existing structure. By a single blow with a hammer, a crystal of ductile metal is instantly transformed, so that its mechanical properties are as completely changed as if the metal had been converted into a new compound by alloying. This transformation certainly does not depend on the presence of foreign substances or of mixed constituents, for the property of hardening is not in the least diminished by the most careful purification of the metal. It is quite as marked in the purest specimens as in those which are much less pure.

The observations which follow were made with the object of defining more accurately the temperature range over which crystallisation and the striking changes in physical properties which accompany it take place in metals in the hardened state. The specimens used were obtained from the same sources as those used in the earlier researches. The gold had a purity of **9997**, the copper of 9993, and the silver of 10,000.

The Crystallisation Temperature of Hardened Gold.

The crystallisation of various ductile metals has been studied, but the most complete series of observations has been made on gold, partly because it does not oxidise or tarnish on heating, and partly because it is rather less difficult to develop the crystalline structure by etching in gold than in silver or copper.

Specimens from the hard-drawn gold wires prepared in the earlier experiments, and having the micro-structure shown in figs. 2 and 3, were ground and polished and were then heated in an air bath for one hour at temperatures ranging from 195° to 335°. They were afterwards etched in warm *aqua regia* in which a good deal of gold had already been dissolved. The microscopic examination of the etched specimens was made by normally reflected light with lenses of 0·65 and 0·95 N.A. These lenses were preferred to the immersion lens of 1·4 N.A. on account of their greater depth of focus. Depth of focus was specially important, as the etching was conducted so as to bring out the crystalline grains in relief, and not merely as the traces of geometrical figures on a perfectly flat field. This relief was brought more clearly into view by giving to the illuminating beam a slight obliquity, so that there was a considerable play of light and shadow among the different

crystalline facets. In tracing the changes of structure brought about by heat, attention was directed, firstly, to the disappearance of the strained type of structure (figs. 2 and 3) and, secondly, to the appearance of a new crystalline structure (figs. 5 and 6).

Microscopic appearance of the etched specimens :—

1. Heated for 1 hour at 195°.   Distorted grains unchanged (figs. 2 and 3).
2. „   „   215°—219°.   Distorted grains still unchanged.
3. „   „   225°—230°.   „   „   disappearing.
4. „   „   258°—267°.   New crystalline masses but no grains.
5. „   „   278°—284°.   Well-formed crystalline grains (fig. 5).
6. „   „   320°—330°.   „   „   „

Fig. 5 shows the structure of No. 5 at a magnification of 700 diameters. The differently oriented grains and lamellæ can be distinctly traced on the photograph, but were of course much more plainly seen in the microscope, as the natural advantage of the accommodation of the eye, as well as the power of rapidly focussing the microscope from one plane to another, have to be sacrificed when the image is received directly on the photographic film.
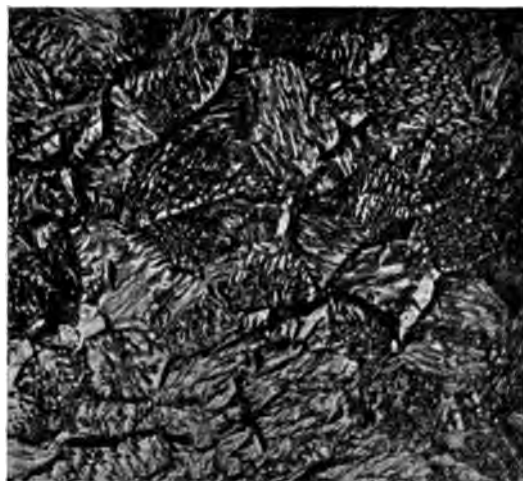
· FIG. 5.—Magnification × 700.
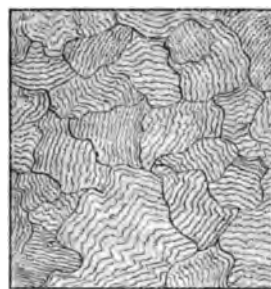
FIG 6.

A diagrammatic sketch of this structure is, therefore, given on fig. 6 for comparison with the similar sketch of the distorted structure.

This great change of structure has been brought about in the solid metal at a temperature 800° below the liquefying point and by a temperature rise of only 50°.

The disappearance of the distorted structure which set in about 225° was clear and unmistakable, as was also the appearance of the definitely oriented

crystals at 278°. The intermediate changes of structure were more difficult to follow, but the impression gained from frequent re-examination of the specimens was that regular orientation sets in from many centres simultaneously, the oriented units being small but numerous. As the kinetic energy of the molecules rises with the temperature, the larger of these units impress their own orientation on their smaller neighbours, and thus absorb them. This process of growth is only arrested when the smaller units have all been absorbed and the surfaces of the larger crystal grains are in contact with each other. With each rise of temperature a new state of equilibrium among the grains is quickly established, and no re-adjustment of their various spheres of influence takes place thereafter till the kinetic energy of the molecules is again increased by a further rise of temperature. The exact conditions of crystalline growth at higher temperatures have not been studied, but there are definite indications that growth and re-adjustment of equilibrium may continue at temperatures considerably above 300°.

The Effects of Heat at Various Temperatures on the Mechanical Stability of Hard-drawn Wires.

The term " mechanical stability " is used here in preference to the more specific terms " hardness " or " rigidity." It has been shown that wire-drawing can be carried to a point at which a certain condition of mechanical stability is reached, so that the wire will break practically without further extension, if a sufficient stress is applied. The ductile metals show their highest tenacity when they are in this condition, and, owing to the relatively small amount of molecular slipping or displacement which occurs before fracture, it may be accepted that the rigidity and the tenacity break down practically at the same point. This state of stability, therefore, supplies a definite and convenient starting point from which to measure any reduction in stability which may result from heating the hardened metal at various temperatures. For the purpose of the present research it was decided to measure the alterations in stability, not by the " yield-point " as usually understood, but by the stress required to produce a permanent extension of 1 per cent. The standard extension was fixed at this amount only after considerable experience on the behaviour of hard-drawn and annealed wires had been accumulated in this and previous researches. The results obtained by its use show that while considerable irregularity is found in the earliest beginnings of yielding, yet after a 1-per-cent. extension is reached the strain responds fairly promptly and regularly to changes of stress.

The oven in which the hard-drawn wires were heated consisted of a thin

steel tube about 5 mm. in diameter and 1 metre long, through which a current up to 125 ampères could be passed. The current was regulated by a water-cooled resistance, while the temperature of the tube was watched by means of a thermo-electric pyrometer. The uniformity of the temperature along the tube was tested once for all by moving the thermo-couple from end to end and noting the temperature. In this way it was found that, with the exception of a short distance at either end, the temperature was practically uniform throughout. The wires annealed were 500/600 mm. long; they were slipped into a thin glass tube which in turn was slipped into the steel tube so as to occupy its middle portion. I am indebted to Mr. Frederick Soddy for the suggestion of this method, and for fitting up for me the necessary apparatus in which it could be carried out.

As the available supply of silver wire of uniform quality was, in the first instance, all required for the E.M.F. tests, the principal series of stability tests were made with gold and copper, but after the conclusion of the E.M.F. observations a few stability tests were made with silver wire.

The hard-drawn gold wire had a tenacity of 14·6 tons per square inch; this corresponded with an actual load of rather over 13 lbs. on the wire. Under this load the wire stretched less than 0·3 per cent., and then yielded no further. The load of 13 lbs. was then applied to wires which had been heated at 30°, 100°, and 200°, and in no case did the extension exceed 0·3 per cent., the stability, therefore, was still unimpaired. A wire which had been heated at 225° was loaded with 12¾ lbs., and stretched 0·7 per cent. From the behaviour of the next wire after heating at 235°, it was judged that the 225° wire would have stood the full load of 13 lbs. without stretching more than 1 per cent. The 235° wire was gradually loaded with 12 lbs., and only stretched 0·3 per cent., but on increasing the load to 13 lbs. it broke without any general stretching. The measurement of the broken pieces showed an extension of rather less than 1 per cent. While the last two wires fully conformed to the arbitrary standard of stability, their behaviour indicated that a slight impairment of stability had set in. The 250° wire was gradually loaded to 13 lbs., and stretched exactly 1 per cent. The 260° wire showed the first failure to reach the full standard; it was gradually loaded to 12 lbs., and stretched 1 per cent. The 270° wire broke at 11·6 lbs., and the measurement of the pieces showed that it had stretched 1 per cent. The 280° wire, gradually loaded to 11 lbs., stretched rather less than 1 per cent., but when the load was increased to 11½ lbs. it stretched rapidly and broke. The measurement of the pieces showed an extension of 5 per cent., of which 4 per cent. had occurred under the last

½ lb. of load. It is to be noted that this serious reduction of stability occurred at 280°, which is the temperature at which well-developed crystalline grains were first visible (fig. 5). The 300° wire stretched 1 per cent. with a load of 5½ lbs., and the 355° wire gave a similar extension at 4 lbs. The latter is equal to a stress of 4·55 tons per square inch ; the stability has thus fallen to less than one-third of its original value, the chief part of the reduction having occurred under an increase of 100° in the annealing temperature.

The tests with copper wires showed the unexpected result that hardened copper begins to lose its stability at a lower temperature than gold, and that the loss proceeds much more quickly thereafter. The full load of 21 lbs., which was still carried by the wire at 200°, had to be reduced to 19 lbs. for the 210° wire, though at this point the extension was rather less than 1 per cent. With the 230° wire a load of 11 lbs., or little more than half the original load, produced an extension of 1·1 per cent. A minimum load of 6 lbs. was reached by the 305° wire ; thus the stability had fallen to 0·28 of its original value under an increase of less than 100° in the annealing temperature. The stability curves of gold and copper (figs. 8 and 9) are shown in an inverted position for more convenient comparison with the E.M.F. curve (fig. 7).

Mechanical stability in the foregoing observations refers to that property as it exists in the mass of metal as an aggregate. Up to a certain point the stability diminishes as the crystallisation becomes more complete; but even in the wires annealed at the higher temperatures the size of the crystalline grains is small when compared with the whole cross-section of the wire. It is probable, therefore, that the stability of even the softest aggregate is much higher than that of the individual crystals. In gold, the aggregate stability fell to 4·55 tons per square inch, but it may safely be assumed that this does not represent the minimum stability of the individual crystalline units. This has an important bearing on the behaviour of metals under alternating stresses. When the theory of hardening by flow was first put forward by me in 1904,* it was then pointed out that the theory might be applied to the elucidation of the disintegration of metals under alternating stresses. So far as I am aware, this has never been done, and this application will therefore be shortly developed here.

Wherever the effects of alternating stresses on the micro-structure have been carefully observed, as in the researches on iron and steel of Ewing and Humphrey, and of Stanton, it has been found that the cracks which led to the ultimate destruction of the specimens generally passed through ferrite

* 'Phil. Mag.,' August, 1904.
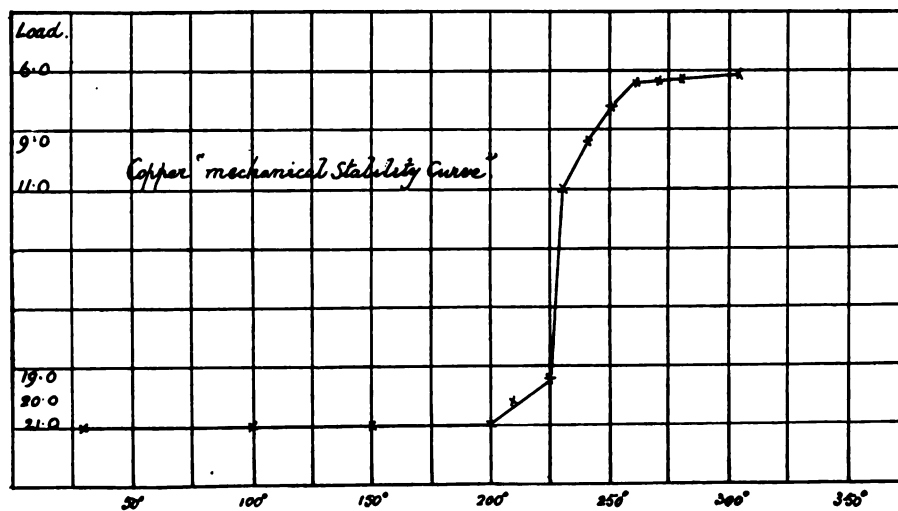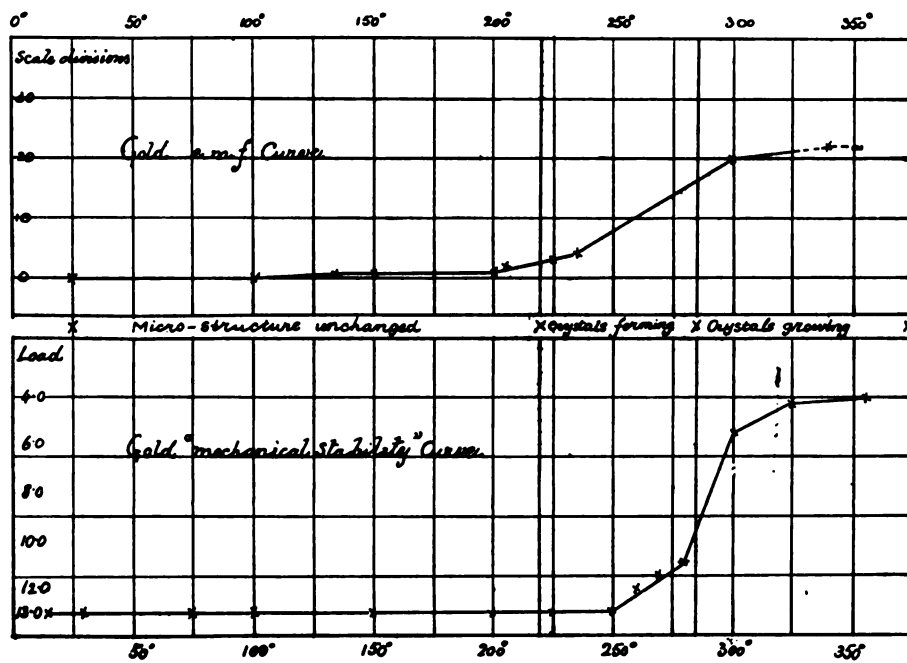
Figs. 7, 8, 9.

grains or areas. Ferrite grains consist of pure iron in its crystalline or softest state. From the analogy of other ductile metals it may be concluded that the stability of the ferrite grains is much less than that of the aggregates

in which they occur, so that a stress which would be insufficient to produce permanent strain in the aggregate would, if it could gain access to them, be more than sufficient to break down these crystalline units.

It is necessary, therefore, to consider in what way disintegrating stresses can gain access to these elements in the mixed structure. It will be shown in the last section of this paper that while the crystalline phase is more perfectly elastic than the hard phase, yet that the amplitude of the vibrations is greater in the latter state. In a reed vibrator the vibrations of the tongue when it is in the hard state are slower but more ample than when it is in the soft state; the hard tongue is less elastic, but more springy. In an aggregate composed of the two phases which is subjected to rapidly alternating stresses, the hard elements may for this reason be able, with safety to themselves, to transmit stresses which will unduly strain the soft elements.

Consider, now, the part played by the mobile phase through which the crystalline passes into the hardened state. In the opening section, the study of the hardened structure, produced by wire-drawing, showed that this structure owes its hardness and stability to the cementing or concreting effect of the flowed metal, while in an earlier paper it was shown that it is possible to overdraw a wire and thus to reduce its hardness and tenacity. *The latter result may be taken to mean that, during the final drawings, the mobile phase was not produced in sufficient quantity to cement together again the surfaces at which slipping had occurred.* Something of the same nature must occur at the surfaces of slip caused by alternating stresses. When the stress is reversed, slip will occur in the opposite direction, but not on the identical plane on which it occurred before, for the cementing action of the hard phase will prevent this. Suppose the second slip to occur at a thickness of one lamella from the first, a new layer of hard phase will be formed at the other face of the intervening lamella, and a sheet of crystalline phase will thus be sandwiched between two hard sheets. The next reversal of stress may find the sandwiched lamella so strengthened that it can resist further slipping. But suppose that one result of the formation of the sandwich has been to leave the crystalline lamella under a slight tension normal to the surfaces, then with each reversal of stress there will be further slips, and the thickness of the hard sheets will increase at the expense of the crystalline substance. Eventually, if the process continued, and assuming that the tension also continued, the whole of the crystalline material would be used up in thickening the hard sheets, and an incipient crack would develop between them, which, in the absence of further supplies of the mobile phase, every additional slip would rub into greater distinctness.

In fig. 10, these steps are shown diagrammatically.
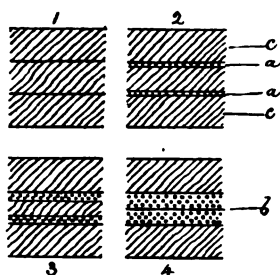
FIG. 10.—1. Unstrained lamellæ in *c* phase.   2. Layers of hard phase *a* formed by slipping.   3. Layers thickened by further slipping.   4. *c* phase all used up and a crack, *b*, developing.

Thermal E.M.F. between Hardened Wires which have been heated at Various Temperatures.

In a former paper* the thermal E.M.F. between silver in its hard and soft states was determined by gradually heating the couple till the maximum deflexion of the galvanometer was reached. The temperature at which this occurred was in the neighbourhood of 250°. It was then realised that this method could only be expected to give satisfactory results if the hard wire of the couple retained its hardness unimpaired till a definite transition temperature was reached. The observations themselves showed that this was not the case. In the newer experiments it was, therefore, arranged that the couples should not be heated above the temperature at which the hard wire would retain its permanent hardness unimpaired. Preliminary experiments showed that by heating to 100° hard wires could be brought into a stable condition while their hardness was only slightly impaired; this was, therefore, selected as the upper temperature to which the couples were to be heated for the development of their thermal E.M.F. The soft wires of the couples were prepared by heating hard wires to various temperatures in the electrical oven already referred to. After heating, it was necessary to handle the soft wires with great care, so as to avoid straining them by bending or twisting. The two wires of the couple were slipped through separate glass tubes, and the junction was made by binding the projecting ends together with very fine silver wire. The junctions with the galvanometer leads were kept at 17°. The couples were heated to 100° by plunging them into a glass tube through which steam was freely blowing at atmospheric temperature; they were cooled by dipping them in water at 17°. The temperature difference for which the E.M.F. was taken

* 'Phil. Mag.,' *loc. cit.*

was thus only 83°, and it was, therefore, necessary to employ a galvanometer of great sensitiveness. The instrument used was of the Kelvin type, and its resistance was 5 ohms. It was adjusted so that each scale-division was equivalent to 0·054 microvolts. This degree of sensitiveness, while amply sufficient for silver, was less satisfactory for gold. With the former a maximum deflexion of 500 scale-divisions was reached, while with the latter the maximum was only 38 divisions. For this reason many more observations were made with silver than with gold, and the E.M.F. curve of the former has been more fully developed and studied.

A number of hard-drawn silver wires were brought into the stable state by hanging them in a glass tube through which steam was blowing freely. Some of these were reserved as standard hard wires, and the others were heated at various temperatures in the electrical oven. In the principal series of observations wires were heated at 130°, 155°, 175°, 200°, 220°, 240°, 260°, 280°, 305°, 325°, and 380°. Each of these wires was tested in a couple with the standard hard wire and in addition the heated wires were tested in pairs among themselves. These latter tests were a useful check on the former. An example will show the extent to which the two sets of observations were in agreement and will at the same time indicate the order of accuracy of the observations as a whole. Let the letters *a*, *b*, *c*, etc., stand for the different couples, then :—

a. 100°—200° heated and cooled between 17° and 100° gave a deflexion of 65 scale-divisions.
b. 200°—220°   „   „   „   „   86   „
c. 100°—220°   „   „   „   „   156   „
d. 200°—240°   „   „   „   „   215   „
e. 220°—240°   „   „   „   „   125   „
f. 100°—240°   „   „   „   „   280   „

Therefore—

f measured in one step	= 280 scale-divisions.
f „ three steps, *a+b+c*	= 276 „
f „ two steps, *a+d*.....	= 280 „
f „ two steps, *c+e*	= 281 „

Observations were made on the effects of heating hardened wires at temperatures below 100° : in these the couples were heated and cooled by plunging them alternately in water at 17° and in melting ice.

With a couple consisting of silver wires in the hardest and softest states respectively, the maximum deflexion obtained for the temperature difference of 83° was 500 scale-divisions, equal to 27 microvolts. This corresponds with an average of 0·09 microvolt per 1° over the whole range. For the different sections of the annealing range the E.M.F. per 1° was as follows :—

From 100° to 200°, 65 scale-divisions = 0·035 microvolt per 1°.
    200° to 220°, 86   „   = 0·232   „   „
    220° to 240°, 125   „   = 0·337   „   „
    240° to 260°, 45   „   = 0·121   „   „

In the diagram (fig. 10) the deflexions have been plotted exactly as they were observed, and no attempt has been made to smooth the curve. The rapid increase of E.M.F. over the crystallising range is sufficiently obvious. The branch curve which starts at 0° and runs up to 200° is the result of E.M.F. measurements with hard wires which had not been brought into the stable condition by a preliminary heating in steam. Considerable irregularity at the lower part of the curve was found among wires which had been drawn at different times. These were traced to secular changes of the same nature as those observed by Muir in his experiments on glass-hard steel. Taken in connection with the other observations, the lower part of the curve suggests that the changes which occur up to 200° are largely due to the relief of strains of this nature, but that above this point a fundamentally different change sets in.

The gold curve of E.M.F. (fig. 7) confirms generally the conclusions drawn from the other observations. It will be noted that the steepest part of the curve corresponds with the temperature range within which complete crystallisation occurs.

Heating Curves of the Hardened Metals.

Repeated attempts have been made to obtain heating curves for hardened silver so as to show the evolution of heat over the transition range, but so far the results have not been sufficiently definite to justify their reproduction here. The researches of Guertler* on the transformation of the silicates and borates from the vitreous to the crystalline state show this heat evolution in a very striking way; but these substances, owing no doubt to their high viscosity and low conductivity for heat, lend themselves to this method of investigation in a way which metals with their low viscosity and high conductivity cannot be expected to do.

Acoustical Tests of the Changes in Elasticity due to Annealing at Various Temperatures.

Reed vibrators were prepared in which the vibrating tongues were made of gold, silver, copper, and iron. These reeds could be fitted on a wind chest and sounded in the usual way by compressed air. The pitch of the notes produced was compared with that of the corresponding notes on a

* 'Zeits. Anorg. Chem.,' vol. 40, No. 2, p. 268.

harmonium, the beats being counted with the help of a stop watch. The
tongues were annealed by placing the *whole* reed in an air bath, for, had the
tongue been removed from the reed for each annealing, there would have
been no certainty that its pitch had not been altered in the subsequent
readjustment. With the metals experimented on, it was found generally
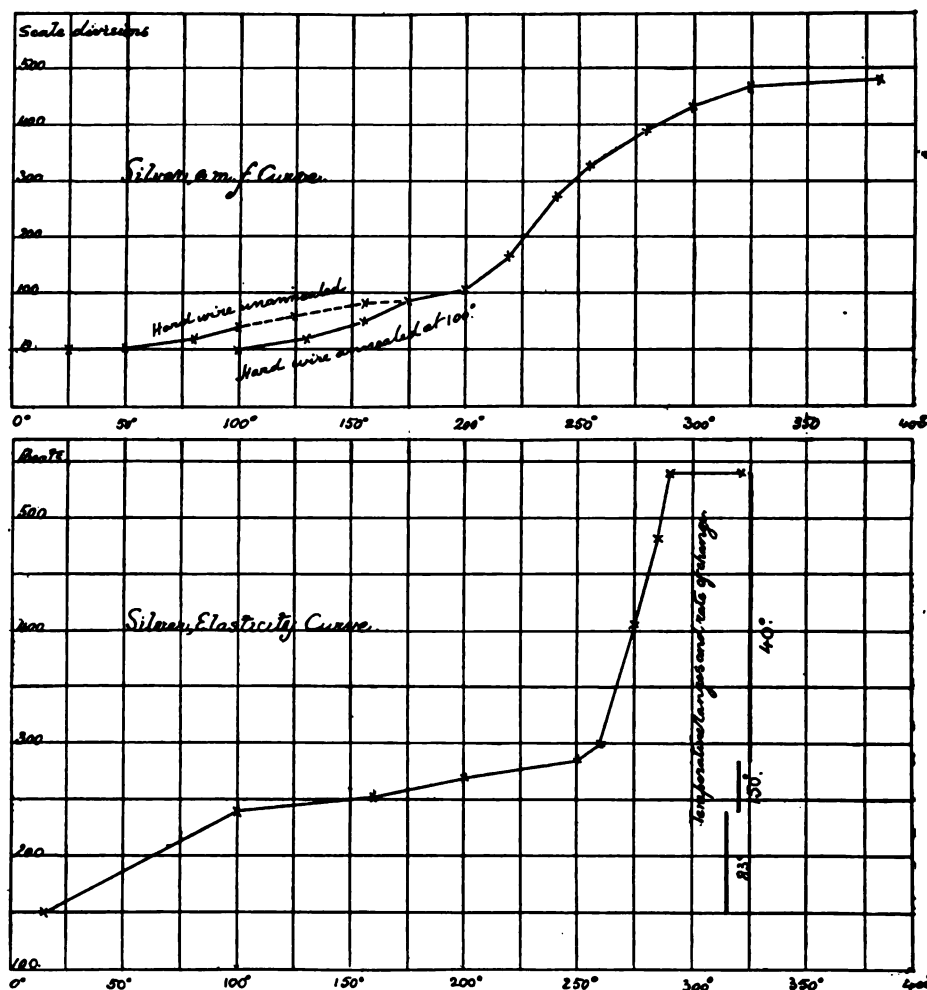
Figs. 11, 12.

that the pitch of the hardened tongue was raised from one to two semitones
by annealing at the crystallising temperature. The pitch of the vibrators
used was in the neighbourhood of G = 195 vibrations per second, so that an
interval of a semitone was equivalent to about 10 beats per second or
600 per minute. As the pitch could be taken either from the note above or

from that below the vibrator note, it was not necessary to count beats quicker than 300/360 per minute, and this could readily be done with a limit of error not exceeding 2 per cent. A syren was tried instead of the harmonium, but for notes of low pitch the latter was found to be superior.

A complete vibration curve for silver is given on fig. 11. The two stages in the relief of strain which are indicated on the E.M.F. curve are here shown much more distinctly. After rising at the rate of about 1 vibration per 1° up to 100°, the rate of increase falls to 0·3 vibration and remains at this rate till 250° is reached. A fresh increase begins at 250°, which develops at 260° into the final very rapid rise of eight vibrations per minute per 1° over the next 30°. At 290° the maximum elasticity is reached, and further heating to 320° produces no increase in the rate of vibration. This method of measurement lends itself particularly well to the study of secular changes of elasticity in newly strained metal; for example, in one instance the rate of vibration of a freshly beaten silver tongue which was kept at the room temperature of 16° rose 30 beats in three hours.

The amplitude of the vibrations of tongues of gold and silver in the crystalline state is very small, owing to the extreme softness of the metal; indeed, unless a small and very thin tongue is used, the stresses caused by the vibrations are sufficient to cause permanent strain. This was first discovered with a gold vibrator. As the annealing temperature was raised, the rate of vibration increased quite normally up to 250°, but at this point the rate suddenly fell back to what it had been at 100°. The annealed tongue was so soft that at first it could only be sounded by a very gentle stream of air; after continued blowing, a portion of its former spring was restored, but with it a lower degree of elasticity. In the case of the silver vibrator, the first tongue used showed the same effect; it was therefore re-hardened by beating it to one-half of its thickness, after which it showed no signs of reverting to the less elastic condition, even after annealing at 320°.

It is my intention to apply this method in a more extended investigation of the elasticity of metals and alloys at their various critical points.

General Conclusions.

1. A number of new observations have been made on the phenomena which are associated with the hard and soft states in metals. Certain of these have referred particularly to the phenomena as they occur in gold, silver, and copper, being a continuation of a research described in a previous paper on "The Influence of Phase Changes on the Tenacity of the Ductile Metals."[*] In the course of that research attempts were made to push the

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[*] 'Roy. Soc. Proc.,' A, vol. 76, p. 462.

process of hardening by wire-drawing to its furthest development, the ideal aimed at being the complete conversion of the metal into the hard or amorphous modification. It was then believed that the maximum tenacity would be reached only when the conversion was practically complete.

It has not as yet been found possible to produce a homogeneous specimen of metal entirely in the hard state, for mechanical working, however severe, of even the purest specimens, always produces a mixed structure consisting of the hard and soft phases. The rigidity and tenacity of the hardened metal appear to depend quite as much on the type of structure developed as on the actual proportions in which the two phases are present.

2. As regards the heat treatment of metals in the hardened state, the temperature ranges over which (1) recrystallisation, (2) loss of mechanical stability, (3) development of thermal E.M.F. between wires in the hard and soft states, and (4) the complete restoration of elasticity in hardened metal occur, are all so well marked, and they coincide with each other so closely, that there can be no doubt that they point to the occurrence of a true change of state in the hardened metal when a certain temperature is reached. The nature of this change of state is shown by the microscope to be a development of the crystalline from the non-crystalline condition.

3. In annealing by heat, no important softening of the metal or reduction of mechanical stability occurs till the recrystallisation temperature is reached, but at that point there is a sharp drop in the stability curve, which drop continues as the temperature of annealing is raised over a range of about 50°. Over this range there is a corresponding growth of the crystalline grains. Above this range the curve flattens rapidly, but there is evidence that the crystals may continue to grow further as the temperature is raised. The mechanical stability diminishes as the crystals grow larger, and it is probable that the true stability of the crystalline phase as it occurs in single crystals is considerably lower than that of any aggregate of crystalline grains.

4. The thermo-electric observations, especially those on silver, show that the thermal E.M.F. is an exceedingly delicate indicator of a state of strain in hardened wires. The observed E.M.F. is therefore in part due to strains of a temporary character and in part to a physical change of state of a fundamental nature. By using as the hard wire of the thermo-junctions a wire which had already been annealed at 100°, these temporary strains were partly eliminated, but the curve obtained still indicated that strains of this type persisted till a temperature of 180° to 200° is reached.

5. The secular changes in hardened metal appear to be limited to the gradual relief of strains similar in kind to the contraction strains observed by Muir in the case of glass-hard steel. This relief of strain differs not

only in degree, but also in kind, from the molecular change which occurs when the crystallisation temperature is reached. The first state is unstable even at ordinary temperatures, while the second is stable up to the lower limit of the crystallisation range. In the first state the relief of strain is not accompanied by any change of micro structure, while in the second a very obvious change occurs.

With reference to these two kinds of molecular constraint in hardened metal, it is now suggested that in the first state the molecules themselves are strained, while in the second state they are merely restrained by their mutual cohesion from turning into a uniformly oriented condition.

6. By using an acoustical test for the detection of minute changes of elasticity in the metal tongue of a reed vibrator, elasticity curves have been obtained which show even more clearly than the E.M.F. curves that the relief of strain by heat occurs in two distinct stages and that the rate of change per degree of temperature is much greater in the second than in the first stage.

7. It is believed that the hardening of metals by chilling from a high temperature is in certain cases due to the development of contraction strains. These strains, if of sufficient magnitude, will lead to the displacement of the molecules from their crystalline orientation at the internal surfaces of grains and lamellæ, thus forming a rigid structure of the mixed phases in the same way as mechanically applied stress would do. From this point of view *the hardening produced by hammering and that produced by chilling are both due to the same kind of molecular change of structure.* The present observations explain for the first time why ductile metals like gold and copper are not hardened when they are chilled from a high temperature. In the case of gold, for example, recrystallisation can occur over the whole range from the solidifying point at 1080° down to the minimum crystallising temperature at 220°. It is clear, therefore, that the contraction strains which occur at any point over this range will immediately be relieved by recrystallisation. In cooling below 220° the contraction is probably too small to give rise to strains of sufficient magnitude to deform the crystals and to produce a hardened condition. From this point of view, a substance with a high crystallising temperature and a high coefficient of expansion is more likely to harden by chilling than one in which these constants are lower.

Substances like the silicates and borates, owing no doubt to their high viscosity, have a comparatively high crystallising temperature; it is, therefore, easy to cool them quickly through the crystallisation range, hence they most naturally pass into the vitreous or amorphous state on cooling. It

would be interesting to ascertain to what extent the hardening of the iron alloys by chilling is due to an increase of viscosity brought about by the added substances.

8. In considering the effects of repeated alternations of stress in metals, it is evident that the endurance of the specimen will be determined not only by the mechanical stability of the aggregate as a whole, but also by the stability of its separate units of structure. In the ductile metals the stability of the crystalline phase is greatly inferior to that of the amorphous phase; this inferiority may at first be completely disguised in a mixed structure composed of the two phases, though it may ultimately make itself apparent under repeated alternations of stress. The present observations indicate why the superior plasticity of the crystalline phase, instead of being in all cases a source of strength in the mixed structures produced by hardening, may actually be an element of weakness.

On Light Elliptically Polarised by Reflexion, especially near the Polarising Angle: a Comparison with Theory.*

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(Communicated by Professor J. Larmor, Sec. R.S. Received January 14,—Read May 23, 1907.)

Taking the phenomena of light to be due to periodic displacements in a rotational ether, we shall investigate the exact character of these displacements in the case of reflection from an isotropic transparent substance. Two well-known vectors play the principal parts in any such optical discussion—the displacement of the medium and its curl; in the electro-magnetic theory the former is proportional to the magnetic force and the latter to the electric "displacement." To give precision to the discussion we shall deal throughout with the displacement of the medium, there being no difficulty in dealing in a similar fashion with the curl.

Let the displacement in the incident light be of unit amplitude and polarised in a plane making an angle θ with the plane of incidence. It can be resolved into two components $\xi = \cos \theta \cos pt$ in the plane of incidence, and $\eta = \sin \theta \cos pt$ perpendicular to this plane. The corresponding components in the reflected beam are then given by the formulae

$$\xi = -R' \cos \theta \cos (pt - \rho') \quad \text{and} \quad \eta = -R \sin \theta \cos (pt - \rho).$$

* [With reference to an oversight in his paper "On Metallic Reflexion," 'Roy. Soc. Proc.,' vol. 77, Jan., 1906, which has recently been pointed out privately by Mr. C. E. Hassé, Prof. Maclaurin writes that he had himself observed it immediately on receipt of the printed paper, but that fortunately the blemish does not invalidate any of the results, beyond requiring a slight modification of the argument in one place.

At the foot of p. 218, in quoting the formula $E = \mu^{-2} \int_0^1 \mu dx$ from the previous paper, the first factor μ^{-2} was left out. When it is inserted, the modulus of E is no longer large, and the following modification becomes necessary. We have

$$r_1 = \frac{A_1 + a_1}{A'_1 + a'_1} = \frac{A_1}{A_1'} \left[1 + \frac{2cd_1 \cos \phi}{\mu^2 \cos^2 \phi - \cos^2 \phi'} \left\{ (E - 1) \mu^2 + (F - E) \sin^2 \phi \right\} \right] ;$$

$$r_2 = \frac{A_2}{A_2'} \left[1 + \frac{2cd_1 \cos \phi}{\mu^2 \cos^2 \phi' - \cos^2 \phi} (E - 1) \mu^2 \right].$$

If both the terms $(E - 1) \mu^2$ and $(F - E) \sin^2 \phi$ are to be retained, we would require two complex constants to specify the layer of transition, which the experimental knowledge would hardly be adequate to determine. When, however, ϕ is small, the term $(F - E) \sin^2 \phi$ will be negligible in comparison with $(E - 1)\mu^2$; and even if ϕ is not small, the first term will not usually be more than one-tenth of the second, the modulus of the factor μ^2 in the latter being large. The neglect of the first term may therefore be expected to produce an error of about one-tenth in the estimated correction due to the layer of transition for large incidences, and practically no error at all for small incidences. This degree of approximation fortunately remains adequate, in relation to the exactness of the data utilised in the argument.]

Here R' and R are given by the sine and tangent formulæ of Fresnel, viz. :—

$$R' = \frac{\sin(\phi-\phi')}{\sin(\phi+\phi')}; \qquad R = \pm\frac{\tan(\phi-\phi')}{\tan(\phi+\phi')},$$

where ϕ and ϕ' are the angles of incidence and refraction, and the upper or lower sign is chosen so as to make R positive throughout. ρ and ρ' are the changes of phase produced by reflection. In the case of an abrupt transition from one medium to the other, ρ' would be zero throughout, while ρ would be zero or π according as ϕ were less or greater than Brewster's angle $\tan^{-1}\mu$. In the more usual circumstances of a gradual transition ρ and ρ' are given very approximately by the formulæ :—[*]

$$\tan\rho = d_1 \times \frac{2\mu^2\cos\phi\,[(F-E)\sin^2\phi-(1-E)\mu^2]}{(\mu^2-1)[\sin^2\phi-\mu^2\cos^2\phi]},$$

$$\tan\rho' = d_1 \times \frac{2\mu^2(1-E)\cos\phi}{\mu^2-1};$$

and the difference of phase $\Delta = \rho-\rho'$ by the formula

$$\tan\Delta = d_1 \times \frac{2\mu^2\{(F-1)-\mu^2(1-E)\}}{\mu^2-1} \cdot \frac{\sin\phi\tan\phi}{\tan^2\phi-\mu^2}$$

$$= -4\epsilon_0 \frac{\mu^2}{(1+\mu^2)^{\frac{1}{2}}} \cdot \frac{\sin\phi\tan\phi}{\tan^2\phi-\mu^2}.$$

Here $d_1 = 2\pi d/\lambda$, where λ is the wave-length in air and d is the thickness of the transition layer; E and F are numbers depending on the law of distribution of the refractive index within the layer, and ϵ_0 is the coefficient of ellipticity at Brewster's angle.

The formula for $\tan\rho'$ shows that it is proportional to $\cos\phi$, so that it will diminish to zero as the incidence increases. In nearly all cases that have been examined E is less than unity and d_1 is a very small quantity. Thus ρ' will be small and positive throughout, approaching the limit zero as the incidence becomes grazing. At direct incidence, where there is no distinction between the plane of incidence and that at right angles to it, ρ is equal to ρ'.

With the substances that are dealt with specially in this paper, and in nearly all cases where the experimental determinations are well assured, ρ increases with the incidence, slowly everywhere except near Brewster's angle, in the neighbourhood of which its increase is very rapid. In such circumstances ρ is greater than ρ' and the crests of the waves representing ξ are reached sooner than the crests of the waves representing η. Thus η, the

displacement perpendicular to the plane of incidence, lags behind ξ, the displacement parallel to that plane, the difference of phase being Δ.*

We have seen that the components of the displacement in the reflected beam are given by

$$\xi = -\mathrm{R}' \cos \theta \cos (pt - \rho') \quad \text{and} \quad \eta = -\mathrm{R} \sin \theta \cos (pt - \rho).$$

If $\theta = 0$ or $\tfrac{1}{2}\pi$, then $\eta = 0$ or $\xi = 0$, so that the reflected light is plane polarised in or perpendicular to the plane of incidence. In other cases, in general, it is elliptically polarised, the elliptic orbit being obtained by eliminating t from the above equations for ξ and η. In this way we obtain as the equation of the ellipse

$$\frac{\xi^2}{\mathrm{R}'^2 \cos^2 \theta} + \frac{\eta^2}{\mathrm{R}^2 \sin^2 \theta} - \frac{2 \xi \eta \cos \Delta}{\mathrm{RR}' \sin \theta \cos \theta} = \sin^2 \Delta.$$

In the special cases of direct or grazing incidence the ellipse degenerates into a straight line. If $\Delta = 0$ the reflected light is plane polarised in an azimuth θ' given by $\tan \theta' = \dfrac{\eta}{\xi} = \dfrac{\mathrm{R}}{\mathrm{R}'} \tan \theta = \epsilon \tan \theta$, while if $\Delta = \pi$ the light is plane polarised in an azimuth θ', where $\tan \theta' = -\epsilon \tan \theta$. These two cases would represent the state of affairs below and above Brewster's angle respectively, if the transition from one medium to the other were abrupt, so that in such circumstances the reflected light would be plane polarised throughout.

By considering the signs of ξ, η, $\partial\xi/\partial t$ and $\partial\eta/\partial t$ in the formulæ above, it appears that the motion in the elliptic orbit takes place in a counter clockwise sense. To give precision to this statement we may express the matter thus:—Look along the ray (whether incident or reflected) in the direction of the propagation of the light. Turn counter clockwise from the plane of incidence through an acute angle θ until the direction of the incident vibrations is reached. The motion in the orbit is then clockwise.†

We proceed to consider the elements of the ellipse referred to above. Putting $\tan \alpha = \epsilon \tan \theta$, the equation of the ellipse becomes

$$\xi^2 \tan^2 \alpha + \eta^2 - 2 \xi \eta \tan \alpha . \cos \Delta = \mathrm{R}^2 \sin^2 \Delta \sin^2 \theta.$$

If ψ be the azimuth of the major axis, we have

$$\tan 2\psi = \frac{2h'}{a' - b'} = \frac{2 \tan \alpha \cos \Delta}{1 - \tan^2 \alpha} = \tan 2\alpha . \cos \Delta.$$

* Of course, if ρ' were greater than ρ, this statement would have to be reversed. Moreover, if we were dealing with the curl instead of the displacement, $(\mathrm{R}\rho)$ would be interchanged with $(\mathrm{R}'\rho')$, so that the component parallel to the plane of incidence would lag behind the other.

† If we were dealing with the curl, instead of the displacement, the motion would be counter clockwise.

The eccentricity (e) is given by

$$\frac{e^4}{(2-e^2)^2} = 1 - \frac{4\,(a'b'-h'^2)}{(a'+b')^2} = 1 - \sin^2 2\alpha \sin^2 \Delta.$$

Putting $\sin 2\gamma = \sin \Delta \sin 2\alpha$, this gives

$$e = \frac{\sqrt{(\cos 2\gamma)}}{\cos \gamma},$$

while for the semi-axes $(a$ and $b)$ we have

$$a = \frac{\text{R} \sin \theta \cos \gamma}{\sin \alpha} \quad \text{and} \quad \frac{b}{a} = \tan \gamma.$$

We shall develop various laws regarding the variation of the elliptic elements from these simple formulæ, and by way of numerical illustration shall apply them to the case of reflexion from diamond and realgar. These substances are selected, because, for them, we have the careful experiments of Jamin to compare with theory, and so to assure us of the firm foundations on which we are building, and also because while their refractive indices are almost identical, their coefficients of ellipticity at the Principal Incidence differ very considerably, so that their comparison should bring into strong relief the influence of this ellipticity. The ellipticity in the case of realgar is abnormally high; it stands near the head of Jamin's list, while diamond occupies a place near the middle. In realgar we shall take $\mu = 2\cdot420$ and $\epsilon_0 = 0\cdot1120$, and for diamond $\mu = 2\cdot434$ and $\epsilon_0 = 0\cdot0242$. This makes $\phi_0 = \tan^{-1}\mu = 67° 33'$ in the case of realgar, and $67° 40'$ in the case of diamond. The difference of phase (Δ) and the coefficient of ellipticity $(\epsilon = \text{R}/\text{R}')$ are then as follows :—

	$\phi = 0.$	10°.	30°.	60°.	65°.	67° 30′.	67° 40′.
Δ (realgar)	0	0° 18′	3° 0′	27° 43′	57° 6′	89° 18′	91° 44′
Δ (diamond) ...	0	0° 4′	0° 39′	5° 54′	17° 18′	77° 26′	90°
ε (realgar)	1	0 ·9750	0 ·7829	0 ·2022	0 ·1343	0 ·1120	0 ·1125
ε (diamond) ...	1	0 ·9750	0 ·7838	0 ·2052	0 ·0749	0 ·0247	0 ·0242

	$\phi = 0.$	68°.	70°.	75°.	80°.	90°.
Δ (realgar)	0	96° 43′	123° 14′	155° 56′	168°	180°
Δ (diamond) ...	0	111° 24′	160° 24′	174° 6′	177° 21′	180°
ε (realgar)	1	0 ·1140	0 ·1352	0 ·2370	0 ·4329	1
ε (diamond) ...	1	0 ·0281	0 ·0699	0 ·2348	0 ·4301	1

These results are represented graphically in figs. 1, 2, 3, and 4 below. In these figures the crosses (×) indicate the results of Jamin's experiments, so that the agreement between theory and experiment is readily estimated.
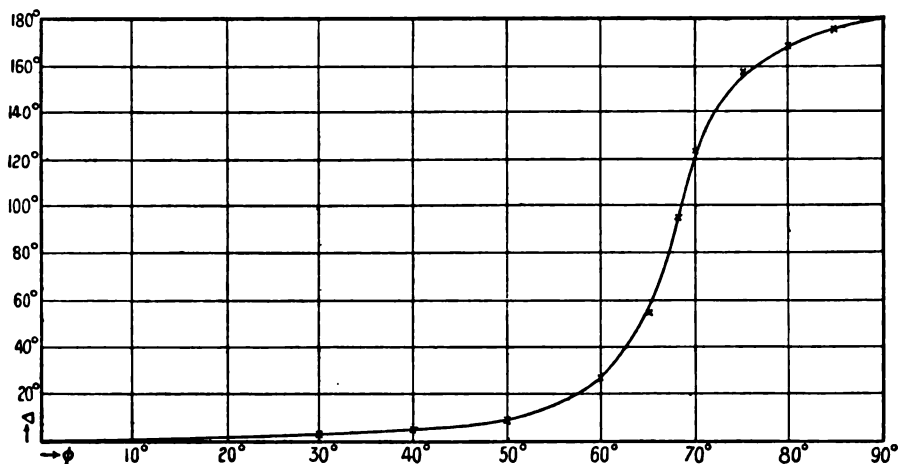
FIG. 1.—Difference of phase for realgar.
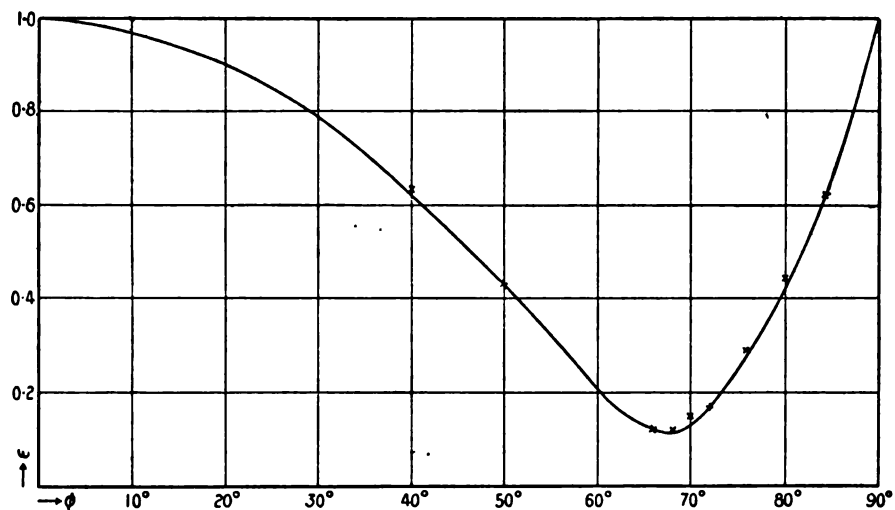
FIG. 2.—Coefficient of ellipticity for realgar.

We have seen that the azimuth of the major axis of the ellipse is given by the formula $\tan 2\psi = \tan 2\alpha \cdot \cos \Delta$, where $\tan \alpha = \epsilon \tan \theta$.

At direct incidence $\epsilon = 1$ and $\Delta = 0$, so that $\psi = \alpha = \theta$; at grazing incidence $\epsilon = 1$ and $\Delta = \pi$, so that $\psi = -\alpha = -\theta$. Thus as the incidence increases ψ will diminish from θ to $-\theta$, and for most azimuths it will pass through the value zero at the Principal Incidence where $\cos \Delta = 0$.
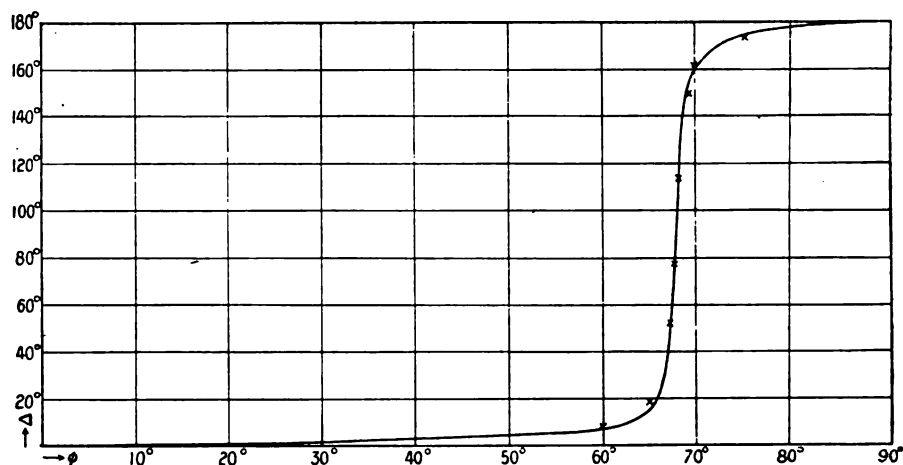
Fig. 3.—Difference of phase for diamond.
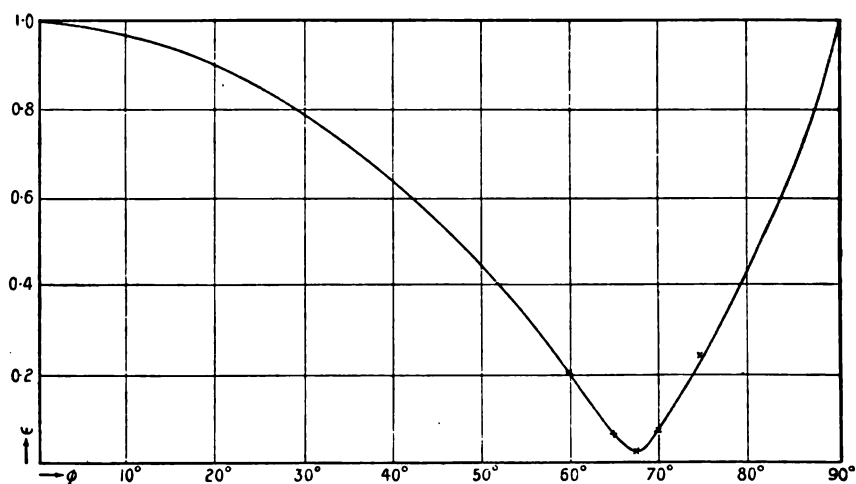
Fig. 4.—Coefficient of ellipticity for diamond.

However, for azimuths greater than $\Omega = 90° - \omega_0$, where $\epsilon_0 = \tan \omega_0$, this will not be the case. In such circumstances $\tan \psi$ will pass through infinity at the Principal Incidence, and ψ will change from $90°$ to $-90°$. Since $\tan 2\psi = \tan 2\alpha . \cos \Delta$, it will be seen that if ϕ be less than the Principal Incidence, $\tan 2\psi$ is negative, and ψ is less than $90°$; while if ϕ be greater than the Principal Incidence, ψ is greater than $-90°$. Hence, for such azimuths the graph for ψ will, in the neighbourhood of the Principal Incidence, have the form represented in figs. 5 and 6 below.

There must, therefore, be some incidences for which the azimuth ψ is a minimum or maximum. To find them we note that ψ is stationary when

$\tan \Delta \cdot \dfrac{d\Delta}{d\phi} = \dfrac{\tan \theta}{\tan \alpha \cdot \cos 2\alpha} \cdot \dfrac{d\epsilon}{d\phi}.$ The minima will be found in the neigh-bourhood of the Principal Incidence (ϕ_0). Putting $\phi = \phi_0 + x$, we have

$$\tan \Delta = A \frac{\sin \phi \tan \phi}{\tan^2 \phi - \mu^2} = \frac{B}{x}(1 + bx + cx^2 + \ldots),$$

therefore

$$\tan \Delta \frac{d\Delta}{d\phi} = -\frac{(1 + bx)}{x(1 + 2bx)}.$$

Also $\epsilon = \epsilon_0 (1 - 2psx + px^2)$. This makes ϵ a minimum when $x = s$, and, as the minimum is very near ϕ_0, s will be very small.

$$\frac{d\epsilon}{d\phi} = 2p\epsilon_0(-s + x);$$

$$\cos 2\alpha = \frac{1 - \tan^2 \alpha}{1 + \tan^2 \alpha} = \frac{1 - \tan^2 \alpha_0 (1 - 2psx + px^2)^2}{1 + \tan^2 \alpha_0 (1 - 2psx + px^2)^2} = \cos 2\alpha_0 (1 + s'x + qx^2),$$

where s' is a small quantity.

Thus the equation for x becomes

$$\frac{1 + bx}{x(1 + 2bx)} = \frac{-2p(-s + x)}{\cos 2\alpha_0 (1 + s'x + qx^2)(1 - 2psx + px^2)}.$$

p is positive, so that for real (small) values of x we must have $\cos 2\alpha_0$ negative. This requires $\alpha_0 > 45°$ and $\tan \theta > \epsilon_0^{-1}$ or $\theta > 90° - \omega_0 > \Omega$.

It is then only for such azimuths that ψ is stationary anywhere.

From the equation $\tan \alpha_0 = \epsilon_0 \tan \theta$ we see that α_0 increases from 45° to 90° as θ increases from Ω to 90°. Hence in this range $\cos 2\alpha_0$ varies from 0 to -1, and we may put $\cos 2\alpha_0 = -2p\kappa^2$, where κ^2 is small when θ is near Ω. The equation for x then becomes

$$x^2 - sx = \kappa^2 (1 - bx)(1 + s'x + qx^2)(1 - 2psx + px^2). \qquad (1)$$

If x, s, and κ be all of the same order of small quantities, then by retaining only the lowest terms in (1) we get $x^2 - sx = \kappa^2$, so that $x = \frac{1}{2}s \pm \sqrt{(\kappa^2 + \frac{1}{4}s^2)}$. One root is positive and the other negative, the positive root being the larger. Thus the maximum beyond the Principal Incidence is somewhat further from that angle than the minimum that occurs before the Principal Incidence is reached.

If s be so small as to be negligible, then $s = s' = 0$ and (1) becomes $x^2 = \kappa^2 (1 - bx)$ on neglecting terms of the fourth order of small quantities.

This gives a positive root, $x = \kappa(1 - \frac{1}{2}b\kappa)$, and a negative root, $x = -\kappa(1 + \frac{1}{2}b\kappa)$. If b be negative, the positive root is numerically the larger; while if b be positive, the negative root is the larger. It will be found that $b = (3 - \mu^2)/2\mu$, so that the sign of b depends on whether μ

is greater or less than $\sqrt{3}$. It will be negative for such highly refringent substances as diamond and realgar, but more usually positive.

If s be not zero, but small compared with x, we get for the positive root of (1) above, $x^2 = \kappa^2 (1-b\kappa)+s\kappa$, so that $x = \kappa+\frac{1}{2}s-\frac{1}{2}b\kappa^2$, and for the negative root $x^2 = \kappa^2 (1+b\kappa)-s\kappa$ and $x = -\kappa+\frac{1}{2}s-\frac{1}{2}b\kappa^2$.

The following tables give the values of ψ for the azimuth $\theta = 89°$ in the neighbourhood of the Principal Incidence for diamond and realgar. It will be seen that the maxima and minima are much nearer the Principal Incidence in the first case than in the second. The figures that follow represent the same results graphically, fig. 5 referring to diamond and fig. 6 to realgar; the scale of ϕ in the former figure being four times that in the latter :—

Diamond.

ϕ.	65°.	67° 30′.	67° 35′.	67° 39′.	67° 40′.
ψ	77° 24′	74° 15′	72° 38′	86° 6′	90° −90°

ϕ.	67° 41′.	67° 45′.	67° 50′.	68°.	70°.
ψ	−86° 17′	−70° 54′	−64° 21′	−69° 21′	−76° 41′

Realgar.

ϕ.	60°.	61°.	62°.	63°.	64°.	65°.	66°.	67° 30′.
ψ	85° 38′	85° 24′	85° 19′	85° 12′	85° 24′	85° 54′	86° 56′	89° 53′

ϕ.	68°.	69°.	70°.	71°.	72°.	73°.	74°.	75°.
ψ	−88° 57′	−87° 2′	−85° 54′	−85° 28′	−85° 24′	−85° 34′	−85° 52′	−86° 9

From these tables and figures it appears that, in the case of diamond, the maximum value of ψ occurs about 10 minutes beyond the Principal Incidence and the minimum about 5 minutes below that angle ; while the corresponding quantities for realgar are 5 degrees and $4\frac{1}{2}$ degrees respectively.

For azimuths less than Ω we have seen that there are no such maxima and minima, and that ψ decreases throughout from θ to $-\theta$ as the incidence increases, and passes through zero at the Principal Incidence. The following
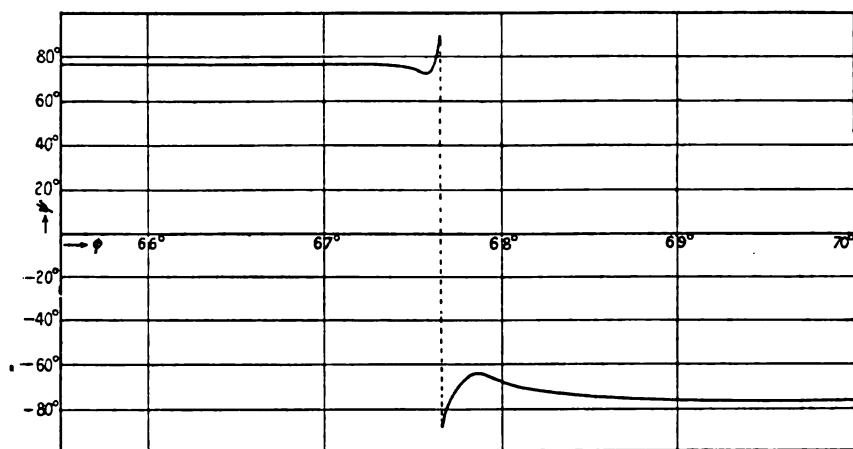
Fig. 5.—Diamond.
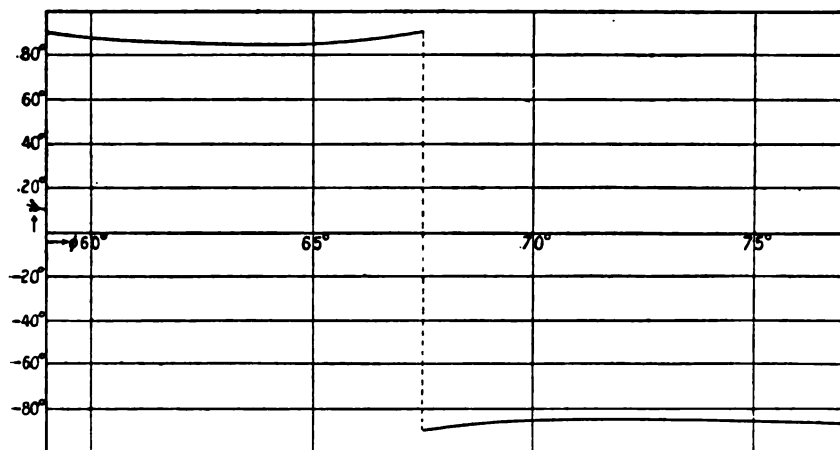
Fig. 6.—Realgar.

table sets out the values of ψ for various azimuths (θ) and incidences (ϕ) in the case of diamond and realgar. The first entry in each case refers to realgar and the second to diamond.

θ.	φ = 10°.	30°.	60°.	65°.	67° 30'.	67° 40'.	68°.	70°.	75°.	80°.
10	9 45	7 52	1 49	0 44	0 1	− 0 2	− 0 8	− 0 45	− 2 12	− 4 16
	9 45	7 52	2 3	0 44	0 3	0	− 0 6	− 0 40	− 2 21	− 4 20
30	29 22	24 19	5 54	2 25	0 3	− 0 7	− 0 27	− 2 28	− 7 8	−13 46
	29 23	24 21	6 45	2 22	0 11	0	− 0 19	− 2 11	− 7 41	−13 56
45	44 16	38 4	10 18	4 14	0 5	− 0 12	− 0 46	− 4 18	−12 19	−23 6
	44 16	38 5	11 30	4 6	0 19	0	− 0 33	− 3 46	−13 9	−23 15
60	59 22	53 36	17 38	7 29	0 8	− 0 21	− 1 23	− 7 36	−21 1	−36 42
	59 22	53 37	19 30	7 5	0 32	0	− 0 57	− 6 31	−22 3	−38 40
75	74 38	71 6	36 3	18 0	0 21	− 0 53	− 8 28	−18 27	−41 10	−58 27
	74 17	71 8	37 25	15 2	1 10	0	− 2 3	−18 32	−41 13	−58 6
85	84 53	83 37	68 21	64 33	88 35	−86 36	−78 11	−64 41	−71 0	−78 48
	79 45	77 19	67 0	40 22	3 48	0	− 6 45	−38 14	−69 42	−78 31
89	88 58	88 44	85 38	85 54	89 53	−89 43	−88 57	−85 54	−86 9	−87 44
	88 59	88 43	85 9	77 24	74 15	90 0	−69 21	−76 41	−85 46	−87 40

These results are exhibited in figs. 7 and 8 below, the first dealing with realgar and the second with diamond.
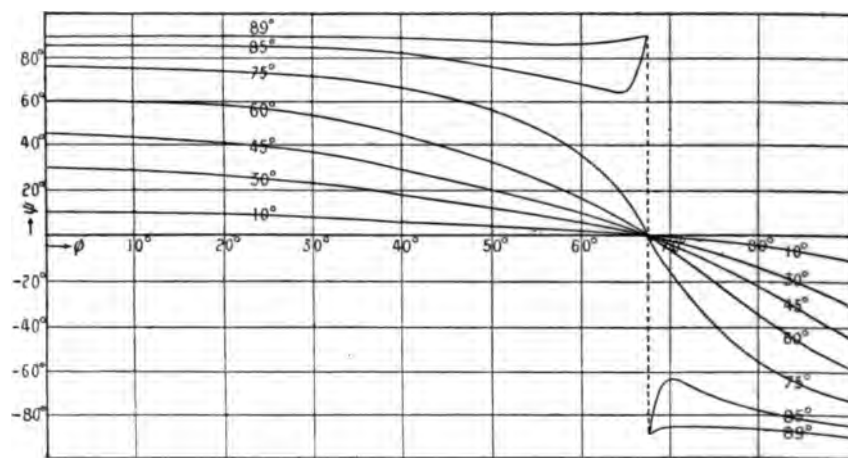
Fig. 7.—Realgar.
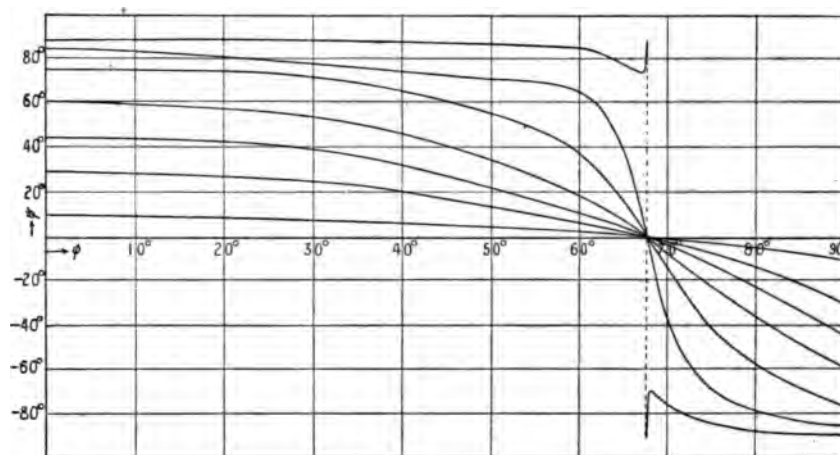
Fig. 8.—Diamond.

We have seen that if the transition from one medium to another were abrupt instead of gradual, the reflected light would always be plane polarised. The azimuth of the plane of polarisation would be α or $-\alpha$, according as the angle of incidence were less or greater than the Principal Incidence. The angle α is given by the equation $\tan \alpha = \epsilon \cdot \tan \theta$, and it must be remembered that ϵ is not the same in the neighbourhood of the Principal Incidence in the two cases of abrupt and gradual transition. Fig. 9 represents an ellipse whose
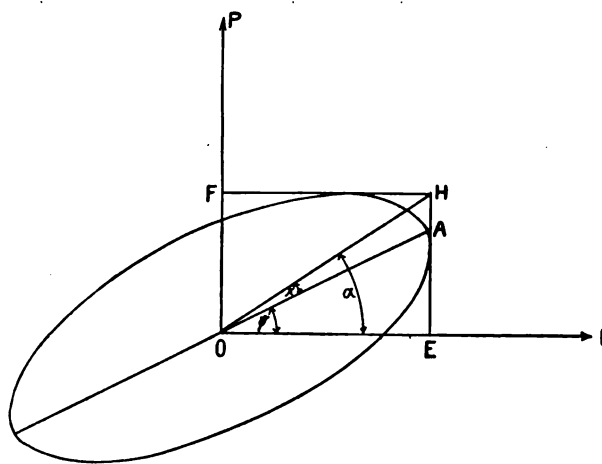
Fig. 9.

centre is O and of which OA is the semi-major axis. OI and OP are parallel and perpendicular respectively to the plane of incidence. EH and FH are tangents parallel to OP and OI respectively. OE represents the amplitude of the displacement parallel to the plane of incidence, and OF the corresponding

amplitude for the perpendicular plane. Thus $OE = R' \cos \theta$ and $OF = R \sin \theta$, tan $HOE = OF/OE = \epsilon \tan \theta$, so that HOE represents the angle α. It will be seen from such a figure, or from the equation $\tan 2\psi = \cos \Delta \times \tan 2\alpha$, that ψ is numerically less or greater than α, according as α is less or greater than 45°. Let χ represent the amount of turning *towards* the plane of incidence in passing from the azimuth of plane polarised light in the case of abrupt transition to the axis of the elliptic orbit when the layer of transition is taken into account. χ will be positive or negative according as α is less or greater than 45°, *i.e.*, according as $\epsilon \tan \theta$ is less or greater than unity. Thus χ will be negative for all angles of incidence when the azimuth is greater than Ω. It will also be negative for high and low incidences, when ϵ is nearly unity, for azimuths greater than 45°; in all other cases it will be positive. At the Principal Incidence, χ is zero for azimuths less than Ω, and 90° for greater azimuths. Thus the layer of transition not only replaces linear by elliptical polarisation, but, when the azimuth exceeds Ω, it turns the direction of the " major axis " from the plane of incidence through a right angle.* It will be seen later that the polarisation is circular at the azimuth Ω, so that there is no discontinuity in passing through that angle. The following table sets out the values of χ for various azimuths and incidences, the first entry referring to realgar and the second to diamond:—

θ.	$\phi = 10°$.	30°.	60°.	65°.	67° 30′.	67° 40′.	68°.	70°.	75°.	80°.
10 {	0	0	0·12	0	0	0	0	0	0·12	0·6
	0	0	0·1	0·2	0	0	0	0·2	0·1	0
30 {	0	0	0·45	0·2	0·1	0·1	0·1	0·3	0·39	0·16
	0	0	0·2	0·7	0·1	0	0·1	0·8	0·2	0·1
45 {	0	0	1·12	0·8	0·1	0	0·1	0·7	1·1	0·19
	0	0	0·6	0·11	0·2	0	0·1	0·14	0·4	0·1
60 {	0	0	1·40	0·25	0·1	0·2	0·4	0·23	1·18	0·10
	0	0	0·5	0·19	0·2	0	0·3	0·23	0·5	0·1
75 {	0	0	0·58	0·23	0·5	0·11	0·38	1·12	0·20	−0·13
	0	0	0·2	0·35	0·6	0	0·5	1·5	0·1	0·1
85 {	0	0	−1·45	−25·17	−87·47	−84·26	−69·34	−24·48	−1·16	−0·13
	0	0	0·5	0·12	0·34	0	0·15	0·23	0·8	0·1
89 {	0	0	−0·33	−9·36	−85·50	−79·1	−51·42	−9·24	−0·22	−0·3
	0	0	−0·1	−0·31	−58·26	−90·0	−39·36	−0·42	−0·1	0

We shall next consider the variation of the quantity b/a, the ratio of the axes, on which the eccentricity of the ellipse depends. We have $b/a = \tan \gamma$,

* See figs. 21 and 22 below.

where $\sin 2\gamma = \sin \Delta \sin 2\alpha$ and $\tan \alpha = \epsilon . \tan \theta$. Thus b/a vanishes when $\theta = 0$ or $\frac{1}{2}\pi$, or when $\Delta = 0$ or π. These, of course, are the cases of plane polarisation, $\theta = 0$ or $\frac{1}{2}\pi$ being azimuths in or perpendicular to the plane of incidence, and $\Delta = 0$ or π being direct or grazing incidence at any azimuth.

For any given azimuth b/a begins at zero for direct incidence, and ends at zero for grazing incidence. It must pass through certain maxima or minima in this interval. From the equation for γ we see that b/a is stationary when $\cos \Delta . d\Delta \sin 2\alpha + 2 \sin \Delta \cos 2\alpha . d\alpha = 0$.

This is satisfied at the Principal Incidence where $\cos \Delta = 0$, and $d\alpha = 0$, since α is stationary with ϵ. As we move in either direction from the Principal Incidence, $\sin \Delta$ diminishes and, for all azimuths less than Ω, $\sin 2\alpha$ increases. For substances such as diamond, for which the variation of Δ is *very* rapid in the neighbourhood of the Principal Incidence, the variation of γ will be mainly controlled by that of Δ, and we shall have b/a a maximum at the Principal Incidence. With other substances, such as realgar, for which the variation of Δ is less rapid, the increase in $\sin 2\alpha$ may more than counterbalance the decrease in $\sin \Delta$. In such circumstances b/a will be a minimum at the Principal Incidence, and there will be two maxima on each side of this and not far from it. Especially with substances of high refractive index, the increase of ϵ beyond the Principal Incidence is much more rapid than its decrease before, so that the maximum beyond the Principal Incidence will be further from it than the one below that incidence. For azimuths greater than Ω, we have $2\alpha > 90°$, so that $\sin 2\alpha$ diminishes with the increase of ϕ. In this case, therefore, b/a diminishes as the incidence increases beyond the Principal Incidence. There can thus be no maximum beyond that incidence, the only maximum possible being one very near the Principal Incidence and below it.

The following tables set out the values of b/a and of the eccentricity (e) for realgar and diamond, and the results for b/a are exhibited graphically in figs. 10 and 11 :—

Realgar.

θ.		φ = 10°.	30°.	60°.	65°.	67° 30′.	67° 40′.	68°.	70°.	75°.	80°.
10°	b/a	0·00047	0·00608	0·01629	0·01978	0·01978	0·01978	0·01983	0·01978	0·01716	0·01571
	c	0·99999	0·99998	0·99989	0·99980	0·99980	0·99980	0·99978	0·99980	0·99984	0·99987
30°	b/a	0·00233	0·01949	0·05387	0·06496	0·06467	0·06496	0·06525	0·06496	0·05474	0·04891
	c	0·99999	0·99982	0·99856	0·99790	0·99793	0·99790	0·99787	0·99790	0·99851	0·99881
45°	b/a	0·00292	0·02531	0·09159	0·11217	0·11187	0·11217	0·11305	0·11246	0·09218	0·07636
	c	0·99999	0·99968	0·99580	0·99369	0·99374	0·99369	0·99475	0·99367	0·99575	0·99710
60°	b/a	0·00233	0·02592	0·14826	0·19227	0·19378	0·19438	0·19589	0·21073	0·14618	0·10069
	c	0·99999	0·997	0·9891	0·9815	0·9811	0·9811	0·9809	0·9774	0·9895	0·9949
75°	b/a	0·00145	0·01600	0·23608	0·38653	0·41728	0·41923	0·42105	0·38888	0·21134	0·09423
	c	0·99999	0·9989	0·9718	0·9221	0·9088	0·9080	0·9069	0·9210	0·9774	0·9956
85°	b/a	0·00120	0·00582	0·17453	0·46843	0·78175	0·77615	0·74810	0·46348	0·13491	0·04046
	c	1	0·9999	0·9847	0·8837	0·6236	0·6306	0·6636	0·8861	0·9908	0·9993
90°	b/a	0	0·00116	0·03088	0·10663	0·16600	0·15511	0·15183	0·10775	0·02997	0·00843
	c	1	0·99999	0·9995	0·9917	0·9879	0·9879	0·9881	0·9931	0·9995	0·99996

Diamond.

θ.		φ = 10°.	30°.	60°.	65°.	67° 30′.	67° 40′.	68°.	70°.	75°.	80°.
10°	b/a	0·00029	0·00145	0·00378	0·00407	0·00436	0·00436	0·00435	0·00435	0·00430	0·00349
	c	1	0·99997	0·99997	0·99997	0·99997	0·99997	0·99997	0·99997	0·99997	0·99997
30°	b/a	0·00036	0·00436	0·01103	0·01280	0·01396	0·01396	0·01396	0·01367	0·01360	0·01076
	c	1	0·99999	0·99993	0·99992	0·99990	0·99990	0·99990	0·99990	0·99991	0·99994
45°	b/a	0·00058	0·00553	0·02037	0·02211	0·02415	0·02444	0·02442	0·02328	0·02298	0·01687
	c	1	0·99998	0·99991	0·99976	0·99971	0·99970	0·99970	0·99973	0·99074	0·99988
60°	b/a	0·00038	0·00553	0·03259	0·03812	0·04191	0·04220	0·04220	0·04016	0·03579	0·02211
	c	1	0·99999	0·99948	0·99928	0·99913	0·99912	0·99912	0·99920	0·99935	0·99976
75°	b/a	0·00029	0·00449	0·04978	0·07753	0·09013	0·09108	0·09101	0·06251	0·05124	0·02066
	c	1	0·99999	0·99876	0·99999	0·99598	0·99598	0·99600	0·99659	0·99870	0·99956
85°	b/a	0·00120	0·00233	0·08725	0·15034	0·27482	0·27607	0·27518	0·16824	0·03346	0·00902
	c	1	0·9999	0·99082	0·98663	0·98141	0·98114	0·98132	0·98576	0·99943	0·99996
90°	b/a	0	0·00120	0·00973	0·03584	0·60068	0·72255	0·56885	0·07929	0·00756	0·00175
	c	1	1	0·99998	0·99781	0·75071	0·69182	0·82264	0·99985	0·99997	0·99990

Fig. 10.—Realgar.

Fig. 11.—Diamond.

On p. 493 are considered the variation of b/a for different incidences at a given azimuth. Its variation for a given incidence at different azimuths is very simply discussed. Under such circumstances ϵ and Δ are given, so that $\sin 2\gamma$ varies as $\sin 2\alpha$, and γ is greatest when $\alpha = 45°$, in which case $\gamma = \frac{1}{2}\Delta$ or $\frac{1}{2}(\pi - \Delta)$, according as the incidence is below or beyond the Principal Incidence. Thus at a given incidence b/a begins at zero with $\theta = 0$, and ends with zero at $\theta = 90°$. It passes through a maximum at the azimuth $\theta = \cot^{-1}\epsilon$, and its maximum value is $\tan \frac{1}{2}\Delta$ or $\cot \frac{1}{2}\Delta$, according as the incidence is less or greater than the Principal Incidence. The following table gives the position and magnitude of the maxima for various incidences:—

φ.	10°.	30°.	60°.	65°.	67° 30′.
θ (realgar)	45° 44′	51° 56′	78° 30′	82° 21′	83° 37′
b/a (realgar)	0 ·00262	0 ·02619	0 ·24686	0 ·54409	0 ·98786
θ (diamond)	45° 42′	51° 55′	78° 24′	85° 43′	88° 35′
b/a (diamond) ...	0 ·00058	0 ·00567	0 ·05153	0 ·15213	0 ·80163

φ.	67° 40′.	68°.	70°.	75°.	80°.
θ (realgar)	83° 35′	83° 30′	82° 18′	76° 40′	66° 35′
b/a (realgar)	0 ·97020	0 ·88888	0 ·54032	0 ·21316	0 ·10510
θ (diamond)	88° 37′	88° 30′	85°	76° 47′	66° 43′
b/a (diamond) ...	1	0 ·68215	0 ·17278	0 ·05153	0 ·02323

These results are represented in figs. 12 and 13 below, the first representing the plan (θ) and the second the elevation (b/a).
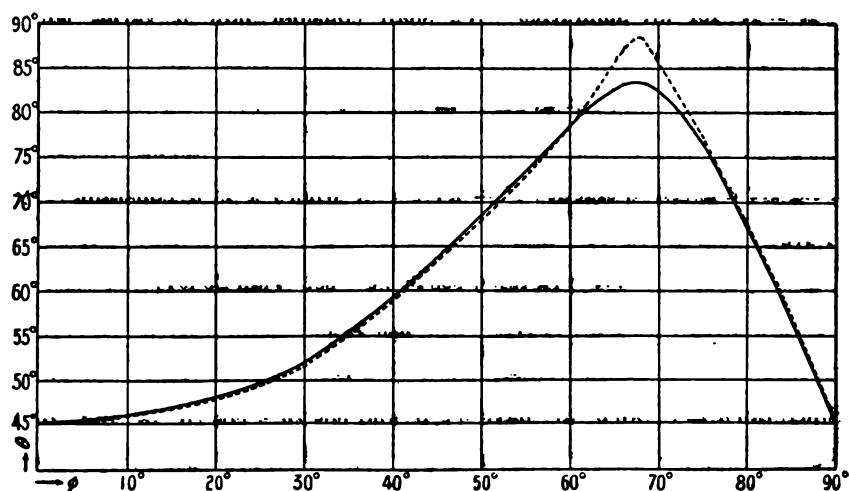
Fig. 12.—The continuous curve represents the results for realgar, the dotted one for diamond.
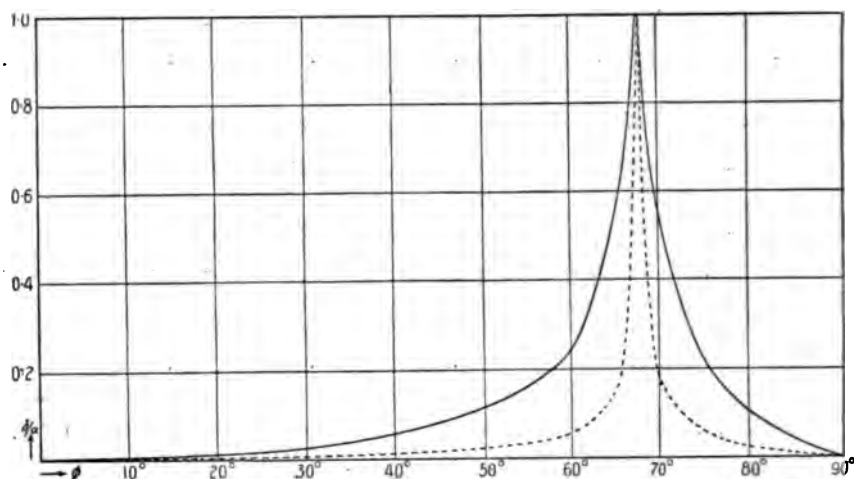
Fig. 13.—The continuous curve corresponds to realgar, the dotted curve to diamond.

The axes of the elliptic orbit are given by the equations

$$a = \frac{R \sin \theta \cos \gamma}{\sin \alpha} = \frac{R' \cos \theta \cos \gamma}{\cos \alpha}$$

and

$$b = a \tan \gamma = \frac{R \sin \theta \sin \gamma}{\sin \alpha} = \frac{R' \cos \theta \sin \gamma}{\cos \alpha}.$$

At direct or grazing incidence we have $\gamma = 0$ and $\alpha = \theta$, so that $a = R = R'$ for all azimuths. We shall consider how a varies with the incidence and azimuth. We have

$$a^2 = \frac{ab}{\tan \gamma} = \frac{R^2 \sin \Delta}{2\epsilon} \frac{\sin 2\theta}{\tan \gamma}.$$

Thus for a given incidence $a^2 = \kappa . \dfrac{\sin 2\theta}{\tan \gamma}$, where κ is a constant. Hence we have

$$\frac{2a\, da}{\kappa} = \cot^2 \gamma \, [2 \tan \gamma \cos 2\theta \, d\theta - \sec^2 \gamma \sin 2\theta \, d\gamma]$$

$$= \cot \gamma . d\theta \left[\cos 2\theta - \frac{\cos 2\alpha}{\cos 2\gamma} \right].$$

Since $\tan \alpha = \epsilon . \tan \theta$, we have $\alpha < \theta$ and $\cos 2\alpha > \cos 2\theta$, 2α and 2θ both being less than π. Moreover, 2γ is never greater than $\frac{1}{2}\pi$, so that $\cos 2\gamma$ is positive and less than unity. Hence if 2α be less than $\frac{1}{2}\pi$, so that $\cos 2\alpha$ is positive, we have $\dfrac{\cos 2\alpha}{\cos 2\gamma} > \cos 2\alpha > \cos 2\theta$; $\cos 2\theta - \dfrac{\cos 2\alpha}{\cos 2\gamma}$ is consequently negative, and a diminishes as θ increases. However, this argument is no longer good when 2α is greater than $90°$. We shall, therefore, proceed to

investigate the roots of the equation $\cos 2\theta = \cos 2\alpha / \cos 2\gamma$. Combining this with $\sin 2\gamma = \sin \Delta . \sin 2\alpha$, we get—

$$\frac{\cos 2\alpha}{\cos 2\theta} = \cos 2\gamma = +(1-\sin^2 \Delta \sin^2 2\alpha)^{\frac{1}{2}},$$

the positive sign being taken, as $\cos 2\gamma$ is positive. For brevity, write $x = \tan^2 \alpha$, $s = \sin^2 \Delta$, $c = \epsilon^2$, so that we have

$$\frac{(1-x)(c+x)}{(1+x)(c-x)} = +\left(1-\frac{4sx}{(1+x)^2}\right)^{\frac{1}{2}},$$

an equation obviously satisfied by $x = 0$, corresponding to $\alpha = 0 = \theta$.

Squaring, and clearing of fractions and of the root $x = 0$, we get

$$x^2(1-c-s)+2scx-c+c^2(1-s) = 0;$$

$$x(1-c-s) = -sc \pm (1-c)\{c(1-s)\}^{\frac{1}{2}}.$$

The process of squaring introduces an irrelevant root. To exclude this the sign of $\frac{1-x}{1+x} \cdot \frac{c+x}{c-x}$ is to be positive, and as $\frac{c+x}{1+x}$ is necessarily positive this requires $\frac{1-x}{c-x}$ to be positive. The value of x given above makes

$$\frac{1-x}{c-x} = \mp \left(\frac{1-s}{c}\right)^{\frac{1}{2}} = \mp \frac{\cos \Delta}{\epsilon},$$

and as $\cos \Delta$ is positive or negative according as the incidence is less or greater than the Principal Incidence, we must take the lower sign below the Principal Incidence and the upper sign beyond it.

Thus below the Principal Incidence we have

$$\tan^2 \theta = \frac{\tan^2 d}{\epsilon^2} = \frac{x}{\epsilon^2} = -\frac{1-\epsilon \cos \Delta}{\epsilon(\cos \Delta - \epsilon)}.$$

But $1-\epsilon \cos \Delta$ is positive, and $\cos \Delta - \epsilon$ is also positive, except very near the Principal Incidence. Hence, except in the immediate neighbourhood of the Principal Incidence, $\tan^2 \theta$ would be negative if a were stationary, so that there is no real value of θ for which a is stationary. Beyond the Principal Incidence our formula gives

$$\tan^2 \theta = \frac{1+\epsilon \cos \Delta}{\epsilon(\cos \Delta + \epsilon)}.$$

The numerator of this fraction is positive and the denominator negative, except very near the Principal Incidence. We see then that da is negative throughout, except in the immediate vicinity of the Principal Incidence, so that a diminishes as the azimuth increases for all incidences outside a small region near the Principal Incidence. This region extends on each side of the Principal Incidence from $\cos \Delta = \epsilon$ to $\cos \Delta = -\epsilon$. Suppose that

$\cos \Delta = \pm \epsilon$ when $\phi = \phi_0 + x$, where ϕ_0 is the Principal Incidence and x is small. We have

$$\tan \Delta = -4\epsilon_0 \frac{\mu^2}{\sqrt{(1+\mu^2)}} \frac{\sin \phi \tan \phi}{\tan^2 \phi - \mu^2} = -2\epsilon_0 \left(\frac{\mu^2}{1+\mu^2}\right)^2 \left(\frac{1}{2} + \frac{2+\mu^2}{\mu}\right),$$

so that

$$\cos \Delta = \cot \Delta \text{ (approx.)} = -\frac{x}{2\epsilon_0} \bigg/ \left(\frac{\mu^2}{1+\mu^2}\right)^2 = \pm \epsilon = \pm \epsilon_0 (1 + px + qx^2),$$

where, as we have seen, p is very small.

This equation gives, very approximately

$$x = \pm 2\epsilon_0^2 \left(\frac{\mu^2}{1+\mu^2}\right)^2,$$

and owing to the smallness of ϵ_0^2 this is usually very small. For diamond we have $x = \pm 2' 55''$ and for realgar $x = \pm 1° 2' 55''$.

At the Principal Incidence a is stationary when $x = 1$, *i.e.*, when $\cot \theta = \epsilon_0$ and $\theta = \Omega$, the azimuth giving circular polarisation. The formulæ for a and b are

$$a = \frac{R \sin \theta \cos \gamma}{\sin \alpha} = \frac{R' \cos \theta \cos \gamma}{\cos \alpha} \quad \text{and} \quad b = \frac{R \sin \theta \sin \gamma}{\sin \alpha} = \frac{R' \cos \theta \sin \gamma}{\cos \alpha},$$

where $\sin 2\gamma = \sin \Delta \sin 2\alpha$.

At the Principal Incidence $\sin \Delta = 1$, so that $\gamma = \alpha$ or $\frac{1}{2}\pi - \alpha$. If $\gamma = \alpha$ we have $a = R' \cos \theta$ and $b = R \sin \theta$, and we must interchange a and b if we take $\gamma = \frac{1}{2}\pi - \alpha$. As a is the greater of the two semi-axes, the first or second of these values must be assigned to γ, according as $R' \cos \theta$ is greater or less than $R \sin \theta$, *i.e.*, according as θ is less or greater than Ω.

Thus, at the Principal Incidence, if θ be less than Ω we have $a = R' \cos \theta$, while if θ be greater than Ω we have $a = R \sin \theta$. Hence, after passing the azimuth Ω, a increases from $R_0 (1 + \epsilon_0^2)^{-\frac{1}{2}}$ to R_0.

It is, therefore, a minimum at the azimuth Ω. It must be remembered, however, that in passing through this azimuth, the angle ψ which the major axis makes with the plane of incidence suddenly changes from $0°$ to $90°$. This means, of course, that the longer axis is perpendicular to the plane of incidence, instead of being in that plane. At the Principal Incidence the axis in the plane of incidence is $R_0' \cos \theta$ throughout, while the axis perpendicular to that plane is $R_0 \sin \theta$. As the azimuth increases, the first axis diminishes steadily from R_0' to zero, while the second increases steadily from zero to R_0.

We have still to consider the variations of a with the incidence for a given azimuth. From the formula for a, viz., $a = R \sin \theta \cos \gamma / \sin \alpha = R' \cos \theta \cos \gamma / \cos \alpha$, we see that when $\theta = 0$, $a = R'$, and when $\theta = 90°$, $a = R$. Thus as the azimuth increases from one of these values to the other, the curve for a must

pass from that representing R', which rises steadily as the angle of incidence increases, to that representing R, which is equal to R' at direct and grazing incidence, but falls to a minimum in the interval at the Principal Incidence.

All these statements as to the variation of a are illustrated in the table and figures that follow. The table gives the values of a for various incidences and azimuths, the first entry referring to realgar, and the second to diamond. Figs. 14 and 15 below represent the same results graphically.

θ.	φ=10°.	30°.	60°.	65°.	67° 30'.	67° 40'.	68°.	70°.	75°.	80°.
10 {	0·4201	0·4613	0·6256	0·6761	0·6950	0·7004	0·7028	0·7224	0·7756	0·8435
	0·4218	0·4641	0·6328	0·6671	0·6984	0·6834	0·6982	0·7310	0·7823	0·8453
30 {	0·4196	0·4421	0·5558	0·5921	0·6122	0·6144	0·6170	0·6359	0·6898	0·7619
	0·4194	0·4541	0·5562	0·5932	0·6156	0·6149	0·6186	0·6362	0·6926	0·7628
45 {	0·4152	0·4171	0·4552	0·4842	0·5005	0·5018	0·5042	0·5205	0·5712	0·6561
	0·4169	0·4196	0·4620	0·4871	0·5018	0·5028	0·5054	0·5212	0·5753	0·6580
60 {	0·4124	0·3912	0·3576	0·3546	0·3538	0·3550	0·3565	0·3658	0·4221	0·5313
	0·4141	0·3937	0·3394	0·3453	0·3551	0·3547	0·3569	0·3703	0·4274	0·5330
75 {	0·4104	0·3712	0·2012	0·1845	0·1832	0·1837	0·1848	0·1979	0·2668	0·4188
	0·4128	0·3737	0·2084	0·1834	0·1841	0·1841	0·1849	0·1962	0·2722	0·4186
85 {	0·4098	0·3645	0·1378	0·0987	0·0789	0·0796	0·0817	0·1069	0·1968	0·3756
	0·4125	0·3717	0·1422	0·0779	0·0619	0·0619	0·0627	0·0809	0·1976	0·3739
89 {	0·4098	0·3637	0·1292	0·0918	0·0792	0·0798	0·0818	0·0995	0·1875	0·3667
	0·4113	0·3659	0·1319	0·0527	0·0179	0·0172	0·0197	0·0528	0·1866	0·3661
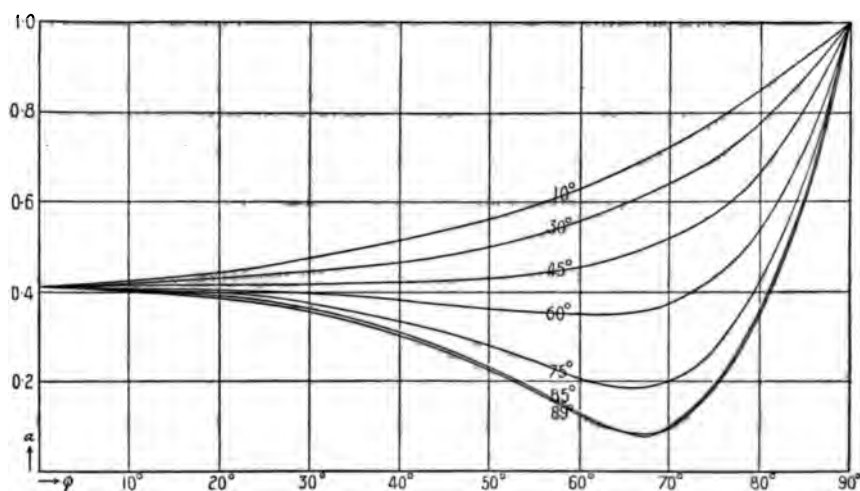
Fig. 14.—Realgar.
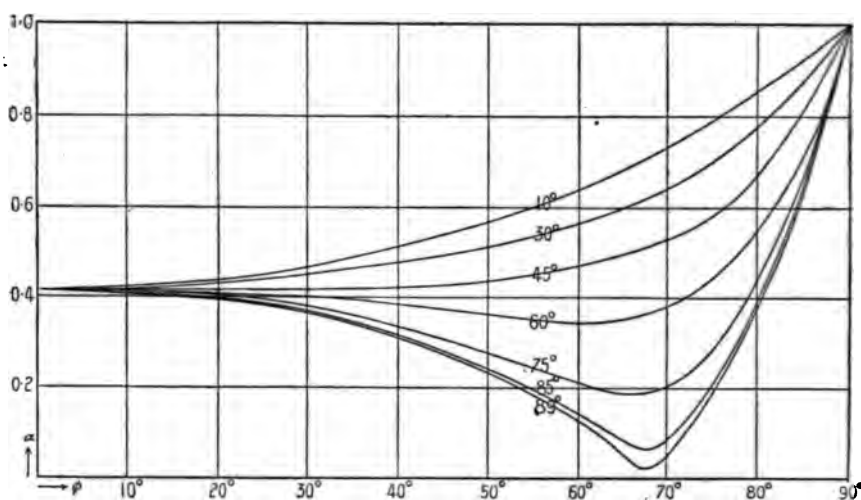
FIG. 15.—Diamond.

We have next to consider the mode of variation of the other semi-axis b, with the incidence and azimuth. The formulæ already obtained give

$$b^2 = a^2 \tan^2 \gamma = (2\epsilon)^{-1} R^2 \sin \Delta \sin 2\theta \tan \gamma = \kappa' \sin 2\theta \tan \gamma,$$

where κ' is a constant for a given incidence. This enables us to discuss the variation of b with the azimuth. We see that b vanishes with γ when $\theta = 0$ and $\theta = 90°$, so that we should expect it to pass through a maximum somewhere in the interval. The above equation for b^2 gives

$$\frac{2b\,db}{\kappa'} = 2 \cos 2\theta \tan\gamma.d\theta + \frac{\sin 2\theta}{\cos^2 \gamma} \cdot d\gamma = \frac{\sin 2\gamma . d\theta}{\cos^2 \gamma}\left[\cos 2\theta + \frac{\cos 2\alpha}{\cos 2\gamma}\right].$$

Thus b is a maximum when $\cos 2\theta = -\cos 2\alpha/\cos 2\gamma$. Except for the change of sign, this is the same equation as that dealt with above on p. 499. It corresponds, in the notation of that page, with the equation

$$\frac{(1-x)(c+x)}{(1+x)(c-x)} = -\left\{1 - \frac{4sx}{(1+x)^2}\right\}^{\frac{1}{2}}.$$

In the present case we require $1 - x/c - x$ to be negative, and, as before, we have

$$\frac{1-x}{c-x} = \mp \frac{\cos \Delta}{\epsilon}.$$

Hence below the Principle Incidence we must take the upper sign, and the lower sign beyond it. We thus obtain

$$\tan^2 \theta = \frac{1 \pm \epsilon \cos \Delta}{\epsilon (\epsilon \pm \cos \Delta)},$$

the upper or lower sign being taken according as the incidence is less or greater than the Principle Incidence. In both cases we get a real value for θ for any given incidence. The magnitude of the corresponding maximum is

$$b = R \sin \Delta (1 \pm 2\epsilon \cos \Delta + \epsilon^2)^{-\frac{1}{2}}.$$

A simple geometrical construction for $\tan^2 \theta$ and the maximum of b is easily obtained. In fig. 16, take $AB = 1$, $AC = \epsilon$, and the angle BAC equal
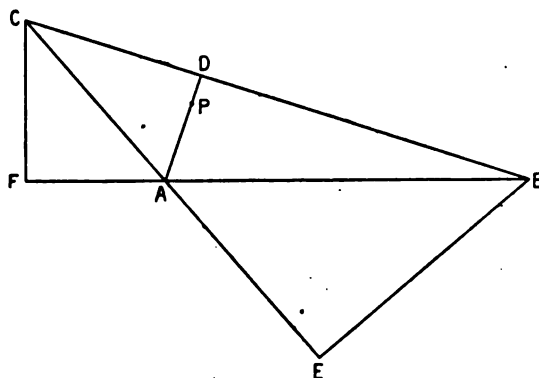
Fig. 16.

to $\pi - \Delta$ or Δ, according as the incidence is less or greater than the Principal Incidence. Draw AD perpendicular to BC, and in it take a point P so that $AP = R' \times AD$.

Then AP represents the maximum value of b, and BD/CD represents $\tan^2 \theta$. To prove this, draw BE and CF perpendicular to CA and AB respectively. Then

$$\sin \Delta (1 \pm 2\epsilon \cos \Delta + \epsilon^2)^{-\frac{1}{2}} = BE/CE = \sin C \quad \text{and} \quad R = \epsilon . R' = R' . AC.$$

Hence

$$b = R \sin \Delta (1 \pm 2\epsilon \cos \Delta + \epsilon^2)^{-\frac{1}{2}} = R' . AC \sin C = R' . AD ;$$

also

$$\tan^2 \theta = \frac{1 \pm \epsilon \cos \Delta}{\epsilon (\epsilon \pm \cos \Delta)} = \frac{BF}{AC . CE} ;$$

but $BF = BF . AB = BC . BD$, and $AC . CE = CD . CB$, so that

$$\tan^2 \theta = BD/CD.$$

The changes in the magnitude of θ and b are readily discussed by means of this construction. As Δ increases from 0 to $\frac{1}{2}\pi$, BC/CD increases from unity. It afterwards diminishes to unity, so that θ increases from 45° to Ω, and then diminishes to 45°. Also, as Δ increases from 0 to $\frac{1}{2}\pi$, AD increases from zero to $\epsilon_0 (1 + \epsilon_0^2)^{-\frac{1}{2}}$, and R' also increases, so that b increases steadily in this range from 0 to $R_0 (1 + \epsilon_0^2)^{-\frac{1}{2}}$. After this AD diminishes to zero. In

the neighbourhood of the Principal Incidence we have $R \sin \Delta = R_\theta$,[*] so that in this region $b = R_0/BC$. As we go from the Principal Incidence, BC increases, so that b diminishes. Thus the maximum value of b is found at the Principal Incidence, and its value is $R_0(1 + \epsilon_0{}^2)^{-\frac{1}{2}}$. The following table gives the position and magnitude of the maximum value of b for various incidences:—

ϕ.	10°.	30°.	60°.	65°.	67° 30′
θ (Realgar)	45° 22′	48° 30′	66° 19′	73° 46′	83° 17′
b (Realgar)	0·0011	0·0107	0·0521	0·0714	0·0786
θ (diamond)	45° 22′	48° 29′	65° 40′	75°	85° 33′
b (diamond)	0·0002	0·0023	0·0112	0·0143	0·0170

ϕ.	67° 40′.	68°.	70°.	75°.	80°.
θ (Realgar)	82° 48′	80° 51′	73° 40′	64° 40′	56° 47′
b (Realgar)	0·0785	0·0783	0·0769	0·0625	0·0539
θ (diamond)	88° 37′	84° 14′	75° 34′	64° 11′	56° 45′
b (diamond)	0·0172	0·0172	0·0161	0·0155	3·0119

The ridge of maxima is represented in plan and elevation in figs. 17 and 18 below.
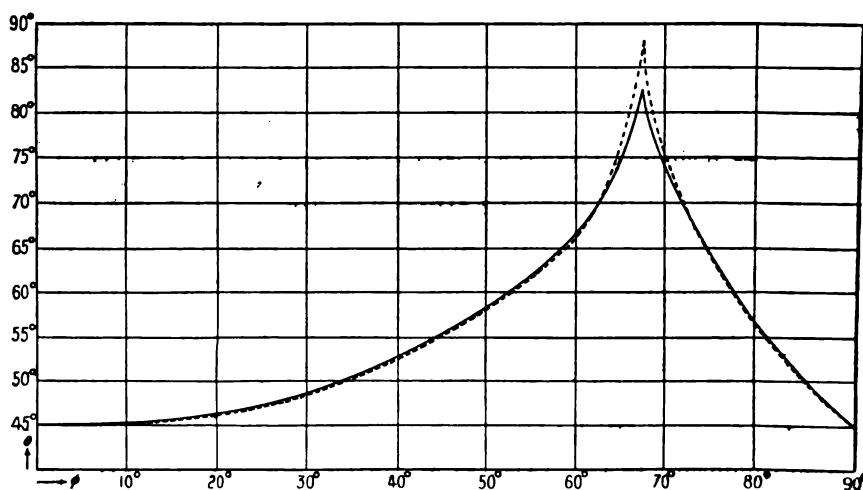
FIG. 17.—The continuous curve refers to realgar, the dotted curve to diamond.

* See 'Roy. Soc. Proc.,' A, vol. 76, 1905, p. 61.
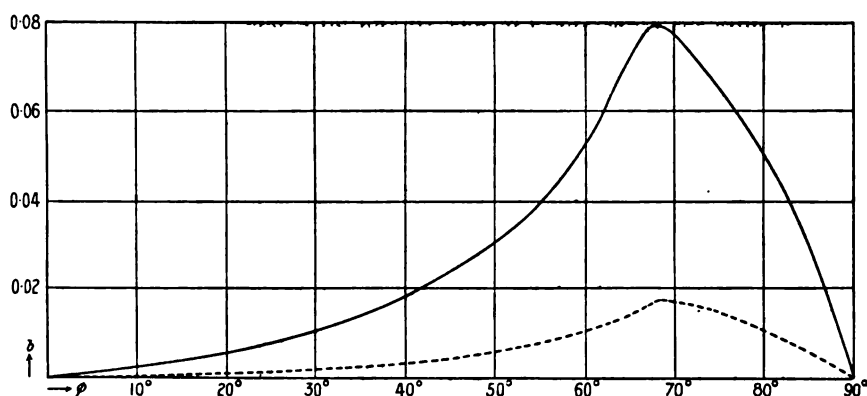
Fig. 18.—The continuous curve refers to realgar, the dotted curve to diamond.

In considering the variation of b with the incidence for a given azimuth, we take $b^2 = (2\epsilon)^{-1} R^2 \sin \Delta . \sin 2\theta . \tan \gamma = \frac{1}{2} R' R \sin \Delta . \sin 2\theta . \tan \gamma$.

As the incidence increases from direct incidence to the Principal Incidence, $R \sin \Delta$ increases throughout, except at the end where it is stationary.[*] Tan γ and R' also increase, so that b increases from zero upwards. When the Principal Incidence is passed, γ decreases again to zero, so that b does likewise. It is evident then that b passes through a maximum between the Principal Incidence and grazing incidence, and that, as the azimuth increases to 90°, the position of this maximum draws closer and closer to the Principal Incidence. The following table gives the values of b for realgar and diamond for various incidences and azimuths :—

θ.	$\phi = 10°$.	30°.	60°.	65°.	67° 30'.	67° 40'.	68°.	70°.	75°.	80°.
10°	0·0004	0·0032	0·0102	0·0134	0·0138	0·0139	0·0139	0·0143	0·0123	0·0082
	0·0001	0·0007	0·0023	0·0027	0·0030	0·0030	0·0031	0·0032	0·0034	0·0026
30°	0·0010	0·0066	0·0299	0·0378	0·0396	0·0397	0·0402	0·0411	0·0378	0·0250
	0·0001	0·0019	0·0056	0·0076	0·0085	0·0085	0·0086	0·0087	0·0095	0·0062
45°	0·0011	0·0106	0·0417	0·0517	0·0560	0·0562	0·0569	0·0585	0·0527	0·0430
	0·0002	0·0023	0·0084	0·0108	0·0118	0·0119	0·0120	0·0124	0·0132	0·0111
60°	0·0010	0·0098	0·0515	0·0632	0·0686	0·0690	0·0698	0·0737	0·0617	0·0480
	0·0001	0·0021	0·0105	0·0131	0·0149	0·0150	0·0150	0·0150	0·0153	0·0119
75°	0·0006	0·0059	0·0475	0·0665	0·0765	0·0770	0·0778	0·0766	0·0564	0·0334
	0·0001	0·0013	0·0104	0·0143	0·0169	0·0168	0·0168	0·0159	0·0130	0·0087
85°	0·0004	0·0021	0·0241	0·0462	0·0617	0·0618	0·0611	0·0495	0·0266	0·0152
	0·0001	0·0009	0·0053	0·0117	0·0170	0·0170	0·0170	0·0136	0·0066	0·0034
89°	0	0·0004	0·0052	0·0100	0·0123	0·0124	0·0123	0·0107	0·0056	0·0039
	0	0·0001	0·0012	0·0035	0·0118	0·0124	0·0112	0·0042	0·0014	0·0006

[*] See 'Roy. Soc. Proc.,' A, vol. 76, 1905, p. 61.

These results are represented in figs. 19 and 20 below.
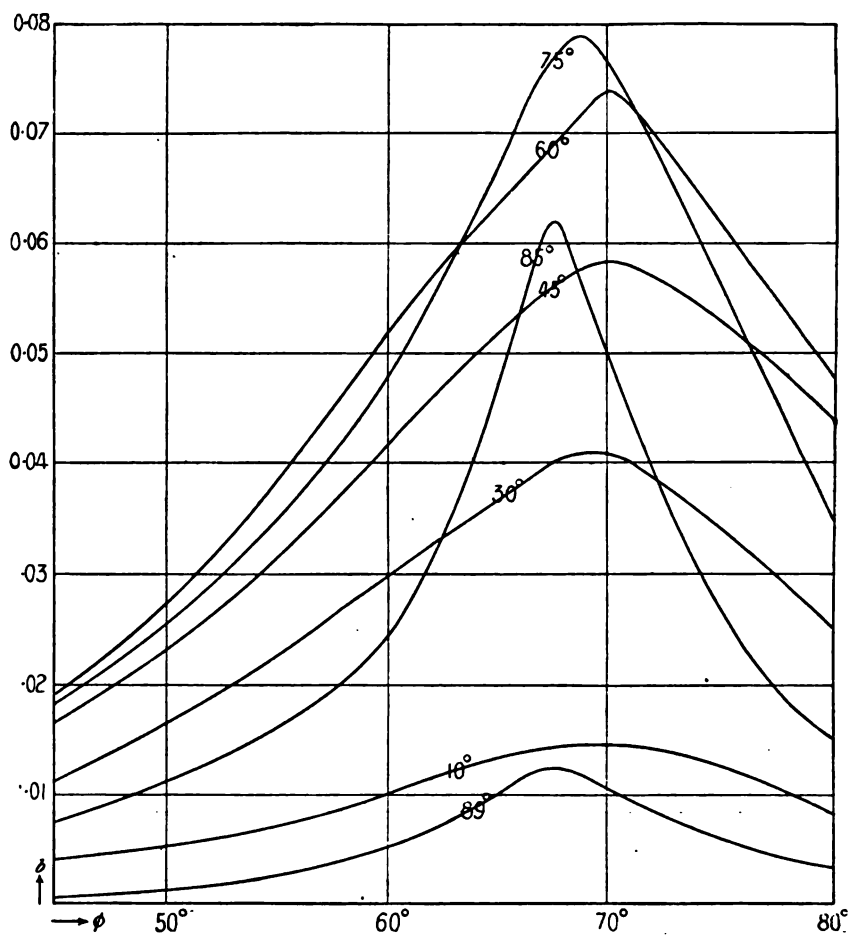
Fig. 19.—Realgar.
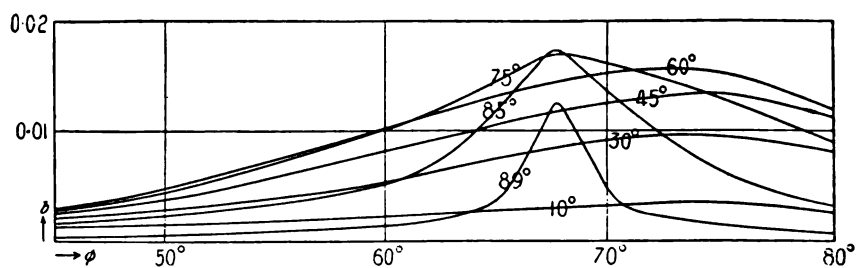
Fig. 20.—Diamond.

The area of the elliptic orbit is

$$\pi ab = (2\epsilon)^{-1} \pi R^2 \sin \Delta \sin 2\theta = \tfrac{1}{2}\pi R'R \sin \Delta \cdot \sin 2\theta.$$
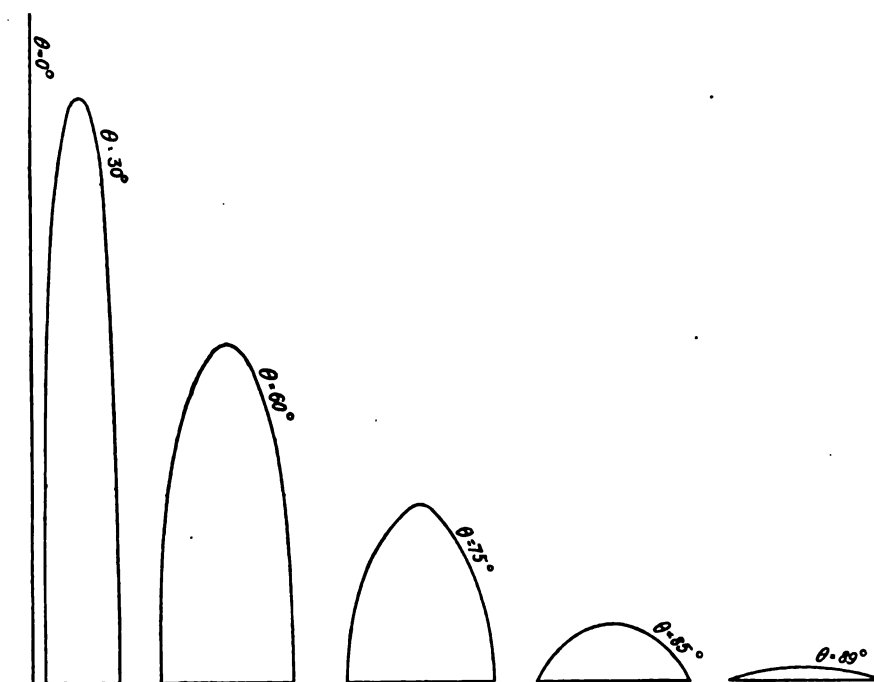
Fig. 21.—Realgar.
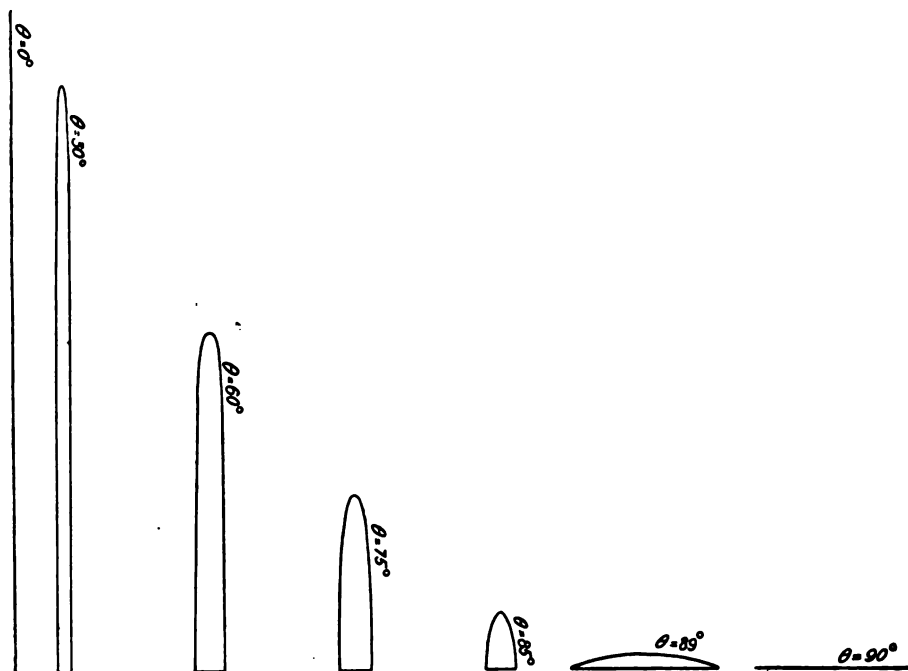
Fig. 22.—Diamond.

For a given incidence this is proportional to sin 2θ, it therefore grows from zero to a maximum when $\theta = 45°$, and diminishes again to zero as θ approaches 90°.

For a given azimuth the area is proportional to R'R sin Δ. As ϕ increases from zero to the Principal Incidence, R' increases, and R sin Δ increases, except near the Principal Incidence, where it is stationary. Hence the area of the ellipse constantly increases within this range. In the neighbourhood of the Principal Incidence R sin Δ is constant, so that the area is proportional to R', and continues to increase throughout a short range beyond the Principal Incidence. When this region is passed, sin Δ diminishes rapidly to zero, so that the area diminishes to zero, passing through a maximum between the Principal Incidence and grazing incidence.

Figs. 21 and 22 represent half of the elliptic orbit, drawn to scale for various azimuths *at the Principal Incidence.*

The Fluted Spectrum of Titanium Oxide.

By A. Fowler, A.R.C.S., F.R.A.S., Assistant Professor of Physics, Royal College of Science, South Kensington.

[Plate 6.]

In a previous paper* it was shown that most of the dark flutings which are characteristic of the spectra of Antarian or third type stars correspond with flutings which appear in spectra obtained from oxide and chloride of titanium, but it was then uncertain whether the flutings originated in the vapour of the oxide or in that of the metal itself.

The purpose of the present communication is to give an account of the observations which have led to the conclusion that the flutings in question are produced by a compound of titanium with oxygen, and to give a revision of the table of wave-lengths based upon photographs taken with increased dispersion.

The Oxide Origin of the Flutings.

The general principle underlying the investigation was the very simple one that if the "Antarian" flutings were due to the *element* titanium they should appear, under favourable conditions, in the spectra of compounds of the metal with different elements, whereas if they were produced by the *oxide* they would only appear when the metal was combined with oxygen, or was able to combine with it during the experiment.

The most decisive results have been obtained from experiments with titanium chloride (TiCl$_4$), a heavy volatile liquid, the vapour of which rapidly combines with oxygen on exposure to moist air and forms dense fumes of titanium oxychloride. On account of this affinity for oxygen, considerable care is necessary in attempting to obtain the spectrum of the chloride without contamination with that of the oxide. The observations have shown, however, that not only is the spectrum of the chloride free from the Antarian flutings, but that it is characterised by a perfectly different group of flutings in the blue which does not occur in the stellar spectra. This "chloride group," as it may be conveniently called for purposes of reference, is a somewhat complicated cluster of flutings fading towards the violet, having three principal heads at wave-lengths 4199·5, 4192·7, and 4188·0, of which the middle one is the brightest.

* 'Roy. Soc. Proc.,' vol. 73, p. 219, 1904.

Experiments with metallic titanium have also indicated that the Antarian flutings are only produced in the presence of oxygen. Particulars of the experiments are as follows :—

(1) Vacuum tubes containing the vapour of titanium chloride were prepared in the usual manner, but it may be remarked that, in consequence of the low conductivity of the vapour, the most satisfactory results were obtained with tubes giving a total length of discharge not exceeding two inches. When the capillary tube was very narrow, little more than a line spectrum was observed, even when there was no jar in the circuit; there was just a trace of the chloride flutings already mentioned, and enhanced as well as arc lines of titanium were well brought out. In the spectrum of the bulb, however, the chloride group was a conspicuous feature, and enhanced lines were not seen, while arc lines were numerous. When a tube of wider bore was chosen, the spectrum of the capillary corresponded very closely with that of the bulb in the previous experiment. In each case, the passage of the jar spark resulted in the appearance of the line spectrum of chlorine and the almost total suppression of that of titanium.

No traces whatever of the Antarian flutings were obtained in these experiments, although the presence of the chloride group of flutings indicated that the electrical conditions in some cases were not unfavourable for their production, if their existence depended only upon the presence of titanium.

(2) The spectrum of titanium chloride was further investigated by introducing some of the liquid into a tube containing dry nitrogen at atmospheric pressure.

A tube 2 cm. in diameter and about 10 cm. in length was sealed at one end and provided with platinum electrodes, having a sparking distance of about 1 cm. Through a rubber stopper at the other end two smaller tubes were passed, one for the admission of any desired gas and the other for the escape of the gas driven out. The admission tube was of ⊢ form, and attached to the vertical arm by a rubber connection was a previously prepared tube containing a small quantity of titanium chloride. This receptacle consisted of a piece of glass tubing about 3 cm. long, drawn out and sealed at its lower end, and scratched with a file so that it might be easily broken; a short piece of rubber tubing was attached at the other end, and when a sufficient quantity of the liquid had been poured in to fill both glass and rubber tube, the latter was closed with a pinch-cock. In this way a sample of the liquid practically free from oxide was secured, and it could be introduced into the sparking tube when desired without further exposure to the external air.

The apparatus having been thoroughly dried by a current of warm dry air,

it was filled with nitrogen, and the titanium chloride was then admitted by breaking off the end of the tube containing it. Even after all the precautions taken to exclude moisture, there was a very slight formation of fumes on the exposure of the liquid, which, however, subsided in a few minutes. On passing the spark (without jar) numerous lines of titanium and the chloride group of flutings were seen, but there was no trace of the Antarian series of flutings. When the jar spark was passed, the chloride flutings were abolished, and enhanced lines of titanium were strongly marked.

To carry the experiment a stage further, the nitrogen was replaced by dry oxygen, and the trace of oxychloride fumes again resulting from residual moisture was allowed to subside. On passing the spark the Antarian series of flutings formed the most prominent feature of the spectrum, but the chloride group was also visible.

(3) A similar experiment in which the sparking tube was filled with dry hydrogen gave an identical result. That is, the chloride group of flutings was visible, while the Antarian series was absent. In this experiment a purple deposit, presumably of titanous chloride (Ti_2Cl_6), was formed on the walls of the tube.

(4) Experiments on the *arc* spectrum of titanium chloride (on iron poles) in an atmosphere of dried nitrogen were also made. Under these conditions, the line spectrum of titanium and the chloride group of flutings were well developed, but the Antarian flutings were excessively feeble and the traces observed were probably due to residual oxygen or moisture, as a thin white deposit was formed on the poles. With an atmosphere of oxygen, however, the Antarian flutings came out strongly.

(5) In another series of experiments, the arc was passed between iron poles, charged with metallic titanium, in an atmosphere of dried nitrogen. Only feeble traces of the Antarian flutings were seen, and these may again be sufficiently accounted for by residual oxygen or moisture. The flutings, however, were well developed when oxygen or air were substituted for nitrogen, but in neither case was the chloride group observed.

(6) As already noted in the previous paper, the Antarian flutings are also visible under the following conditions :—

(*a*) Arc in air between carbon poles well charged with oxide of titanium, the flutings being best seen in the "flame" when the arc is long.

(*b*) Spark, without jar, through fumes of oxychloride of titanium ; with a spark of suitable intensity, the line spectrum is almost eliminated, but there is a continuous spectrum of considerable strength which doubtless arises from particles which are incompletely volatilised.

(c) Oxy-coal-gas flame, fed with the fumes of titanium oxychloride; the
    flutings are in this case not easily seen on account of the bright
    continuous spectrum which is also present.

These observations do not seem to admit of any other conclusion than that
the flutings represented in the spectra of Antarian stars are produced by
a compound of titanium with oxygen, and not by the vapour of the metal
itself.

The result is of some importance as indicating that the source of the fluted
absorption in the Antarian stars is at a temperature low enough to permit
the formation of a chemical compound, and also as demonstrating the
presence of oxygen, of the existence of which in these stars there is other-
wise no direct evidence. The investigation has lately gained additional
interest in consequence of Professor Hale's discovery of some of the less
refrangible flutings in the spectra of sun-spots.[*]

The Wave-lengths of the Flutings.

The identification of the flutings of the Antarian stars with those of
titanium rested upon such a great number of apparent coincidences in
position, and similarity of appearance, that it was almost independent of
a very precise knowledge of the wave-lengths, and was sufficiently justified
by the wave-lengths derived from photographs taken with the moderate
dispersion then available. No further determinations of the positions of
the stellar bands have been published, but the application of a more
powerful spectrograph has made it possible to determine the wave-lengths of
the terrestrial flutings with much greater precision. The instrument
employed was a very efficient one of the Littrow form, having one prism of
$60°$ ($\mu_D = 1.6467$) and a focal length of 12 feet, the effective aperture
employed being $1\frac{1}{2}$ inches. The spectrum is photographed in sections on
plates $12 \times 2\frac{1}{4}$ inches, and the linear dispersion ranges from 16 tenth-metres
per millimetre at $\lambda 7100$ to 2·7 tenth-metres per millimetre at $\lambda 4350$.
With this dispersion the heads of many of the flutings are found to be more
complex than was formerly suspected, but neither this nor the corrections of
the wave-lengths affects the probability of identity with the stellar flutings.

Many experiments have been made in order to produce the fluted
spectrum as free as possible from superposed lines. The uncondensed spark
passed through the fumes from titanium chloride is possibly the best way of
obtaining this result, but the photographic registration with high dispersion
is difficult. The most convenient method yet found is to volatilise titanium

* 'Astrophysical Journal,' vol. 25, p. 75, 1907.

oxide in the electric arc between iron poles, and the photographs reproduced in Plate 6 were obtained in this manner.

Under these conditions, the " line " spectrum of titanium is not strongly marked, and iron is only represented by the brighter lines of its flame spectrum. Nearly all of these metallic lines appear on the more refrangible side of D, and are strongest towards the blue. The flutings which occur in the flame of the iron arc do not appear to contribute appreciably to the combined spectrum of iron and titanium oxide. Incidentally, the photographs admirably illustrate the simplicity of the line spectrum of iron in the arc-flame.

For the determination of wave-lengths, the reference lines employed were those of iron and titanium occurring with the flutings, whenever suitable lines were available for the purpose. In many cases, however, and in the whole region on the red side of D, the reference lines were selected from a spectrum of the iron arc photographed in juxtaposition with the fluted spectrum ; the shutter for exposing the two parts of the slit was entirely detached from the spectrograph, and there was no evidence of relative shift of the two spectra in the plates measured.

The adopted positions of the reference lines were those given by Rowland in his table of solar spectrum wave-lengths, and the interpolation was made in the usual manner by the Cornu-Hartmann formula. For the part of the spectrum less refrangible than 6860, in which Rowland does not tabulate any lines of iron, lines of the arc spectrum were first identified with solar lines and the corresponding solar wave-lengths adopted. The wave-lengths given in the table are stated to two places of decimals, except in the extreme red, where the dispersion is relatively small, and in cases where the edges of the flutings are not very sharply defined.

No attempt has yet been made to tabulate the thousands of fine " structure lines " which compose the flutings, but all the " heads " and " sub-heads " which could be identified as such have been included. Some of the more marked details in the heads, probably consisting of relatively strong structure lines, or clusters of such lines, have also been measured ; for want of a better term, they are described as " maxima." The classification into heads and sub-heads is somewhat arbitrary in many cases, and it should be explained that some of the heads are classed as such, not because they are prominent features of the spectrum, but because of their probable association in series with stronger heads in the groups to which they belong.

With the high dispersion employed, the heads of some of the fainter flutings, especially in the region more refrangible than F, almost lose their distinctive characteristics, and their identification has only been possible in

some cases by comparison with photographs taken on a smaller scale. It has been considered desirable to include these for reference in comparisons with stellar spectra, which are usually photographed with moderate dispersion, and also because of their possible use in investigations of the series relationships of the various flutings.

The relative intensities of the flutings are roughly shown by the numbers in the second column of the table, and an attempt is made in the third column to indicate the general characteristics by symbols having the following significance :—

   (a) The fluting fades out rapidly, and is not clearly resolved with the dispersion employed. These appear as lines with a slight shading towards the red.

   (b) The fluting fades away more gradually, and the structure lines are very closely crowded together.

   (c) The fluting resembles those of class (b), except that the structure lines are more clearly separated.

   (d) The structure lines are widely separated, and extend over a long range.

For convenience of description in the table, the flutings are classed in numbered groups, into which the spectrum seems naturally to divide itself. It is not possible, however, to convey an adequate idea of so complex a spectrum by means of a table alone, and reference should be made to the reproductions of the photographs given in Plate 6. The first four strips, representing the spectrum from 4580 to 7200, have been enlarged 1·8 times from the original negatives, and the attached scale of wave-lengths will facilitate comparison with the table. Lines due to iron are separately indicated, as also are those arising from impurities of sodium, calcium, and lithium in the material employed. The superposition of iron lines on the flutings beginning at 4954·8, 5167·0, and 5448·5, tends to conceal the character of the heads, and reproductions of photographs taken with carbon poles are accordingly given in the fifth strip, the enlargement here being 3·5 times. In this case most of the iron lines are absent, but titanium lines are generally more numerous throughout the spectrum.

The photographs of the less refrangible parts of the spectrum were taken on Messrs. Wratten's " Verichrome " and " Panchromatic " plates, which gave uniformly good results.

The Fluted Spectrum of Titanium Oxide.

Wave-length.	Intensity.	Character.	Remarks.
4353·68	2	*d*	1st head of 14th group.
4395·05	2	*d*	2nd head.
4421·66	1	*d*	Sub-head.
4436·68	2	*d*	3rd head.
4462·34	3	*d*	1st head of 13th group.
4462·70	3	—	A " maximum " in head.
4506·08	2	*d*	2nd head.
4506·62	2	—	A maximum in head.
4548·04	2	*d*	3rd head.
4548·30	2	—	A maximum in head.
4584·62	3	*d*	1st head of 12th group.
4584·92	3	—	A maximum in head.
4586·78	3	*d*	Sub-head.
4587·20	3	—	A maximum in sub-head.
4626·49	4	*d*	2nd head.
4628·68	4	*d*	Sub-head.
4668·82	4	*d*	3rd head.
4669·19	4	—	A maximum in head.
4671·26	3	*d*	Sub-head.
4671·66	3	—	A maximum in sub-head.
4761·08	5	*d*	1st head of 11th group.
4761·37	5	—	A maximum in head.
4761·86	5	—	„ „
4764·52	5	*d*	Sub-head.
4804·55 } 4805·61	5	*d*	2nd head, included in cluster.
4807·42	4	*d*	Sub-head.
4848·20 } 4849·03	3	*d*	3rd head, included in cluster.
4893·00	2	*d*	4th head.
4954·78	6	*d*	1st head of 10th group, sharply defined.
4955·26	6	—	A maximum in head.
4957·21	6	*d*	Sub-head.
5002·88	3	*d*	2nd head ⎱ Identification difficult with high dispersion.
5050·5	3	*d*	3rd head ? ⎰
5167·00	7	*d*	1st head of 9th group, sharply defined.
5167·50	7	—	A maximum in head (not Mg line).
5169·51	7	*d*	Sub-head.
5240·71	5	*d*	2nd head, structure lines very wide apart.
5241·00	5	—	A maximum in head.
5307·92	3	*d*	Sub-head.
5308·14	3	—	A maximum.
5356·21	2	*d*	Sub-head.
5356·86	2	—	A maximum.
5359·07	3	—	A maximum, or ? sub-head.
5359·51	2	—	A maximum.
5361·22	3	—	„
5391·05	2	—	A maximum, or ? sub-head.
5448·48	7	*d*	1st head of 8th group, sharply defined.
5449·07	7	—	A maximum in head.
5451·32	7	*d*	Sub-head.
5496·79	5	*d*	2nd head.

Wave-length.	Intensity.	Character.	Remarks.
5597 ·92	10	*a*	1st head of 7th group, sharply defined.
5603 ·98	5	*b*	Sub-head.
5629 ·53	8	*a*	2nd head.
5635 ·54	5	*b*	Sub-head.
5661 ·68	6	*a*	3rd head.
5667 ·81	4	*b*	Sub-head.
5694 ·56	5	*a ?*	4th head.
5728 ·13	4	*a ?*	5th head.
5760 ·15	4	*b*	1st head of 6th group (followed by Ti 62 ·48 and Fe 63 ·22).
5790 ·86	4	*b*	Sub-head.
5811 ·28	4	*b*	2nd head.
5815 ·14	4	—	A maximum, or line.
5846 ·70	4	*b*	Sub-head.
5863 ·55	4	*b*	3rd head (probably).
5872 ·9	3	*b*	Sub-head.
5905 ·1	3	*b*	,,
5954 ·66	3	*b*	1st head of 5th group (relatively inconspicuous).
6006 ·5	3	*b*	2nd head.
6057 ·6	2	*b*	3rd head.
6149 ·2	5	*a ?*	A doubtful head.
6158 ·86	10	*a*	1st head of 4th group.
6162 ·37	8	—	Sub-head ? Perhaps wholly Ca line.
6174 ·60	10	*a*	2nd head.
6183 ·83	4	*b*	Sub-head.
6186 ·77	8	*a*	3rd head.
6190 ·07	5	*b*	Sub-head.
6215 ·35	8	*a*	4th head.
6222 ·72	6	*b*	5th head.
6268 ·35	4	*b*	Sub-head.
6275 ·70	3	*b*	,,
6321 ·0	2	*c*	,,
6321 ·8	2	—	A maximum in sub-head.
6350 ·6	2	*b*	Sub-head.
6357 ·9	3	*c*	1st head of 3rd group (relatively inconspicuous).
6384 ·4	3	*c*	2nd head.
6400 ·1	2	*b*	Sub-head.
6416 ·0	3	*b*	3rd head.
6448 ·2	4	*b*	4th head.
6479 ·4	4	*b*	5th head.
6484 ·0	4	—	Sub-head ? or cluster of lines.
6512 ·8	4	*b*	6th head.
6544 ·5	4	*c*	7th head.
6550 ·2	4	—	A maximum.
6551 ·8	4	—	,,
6562 ·5	3	*c*	Sub-head.
6579 ·5	3	*c*	,,
6594 ·5	3	—	A maximum.
6626 ·3	3	—	,,
6634 ·4	3	*b*	Sub-head.

Wave-length.	Intensity.	Character.	Remarks.
6651 ·5	8	*b*	1st head of 2nd group.
6681 ·0	8	*b*	2nd head.
6714 ·1	8	*b*	3rd head.
6748 ·0	8	*b*	4th head.
6782 ·0	8	*c*	5th head.
6815 ·1	5	*c*	6th head.
6850 ·0	5	} *c*	7th head.
6852 ·5	5		
6883 ·8	4	*c*	8th head.
6919 ·4	4	*c*	9th head.
6951 ·8	2	*c*	10th head.
6988 ·8	2	*c*	11th head.
7054 ·5	10	*a*	1st head of 1st group.
7059 ·6	4	*b*	Sub-head.
7087 ·8	10	*a*	2nd head.
7092 ·9	4	*b*	Sub-head.
7125 ·5	10	*a*	3rd head.
7130 ·6	4	*b*	Sub-head.
7158 ·9	3	*a*	4th head ?
7197 ·7	2	*a*	5th head ?

Reference to Stellar Bands.

The use of greater dispersion has removed the doubt as to the agreement of the 7th group of flutings with Dunér's stellar band No. 4, to which reference was made in the former paper. It is now evident that the appearances described as "lines" near 5598, 5630, and 5662 are really the heads of short flutings of class *a*, as might have been suspected from the near equality of the intervals separating them from the weaker but more obvious flutings (when seen with small dispersion) at 5604, 5636, and 5668. This group, therefore, begins with the fluting at 5597·9, and there is no longer any uncertainty as to its general correspondence with the stellar band, for which Father Sidgreaves gives the wave-length 5597.

Evidence as to the presence in stars of the first group of titanium oxide flutings, beginning at 7054·5, is afforded by the recent photographs of the spectrum of Omicron Ceti taken by Mr. Slipher, of the Lowell Observatory.* It is stated that "the star spectrum stops so suddenly at λ 7040 as to leave little doubt that another of these bands begins at that point and outruns the sensitiveness of the plate into the red." There can be no doubt that the abrupt ending to which reference is made owes its origin to absorption by the 7054·5 group of titanium flutings. Still more recently, Mr. Newall has informed me that he has identified the three heads of the 7054·5 group in photographs of the spectrum of α Orionis.

* 'Astrophysical Journal,' vol. 25, p. 236, April, 1907.

All the stronger groups of flutings have accordingly now been traced in stars, and it may be assumed that the fainter flutings of groups 3, 5, and 6 will also be present when the banded spectrum is well developed, as in α Herculis and ο Ceti.

It still seems improbable, however, that titanium oxide can sufficiently account for all the stellar bands. As remarked in the former paper, the stellar intensities of Dunér's bands 1 and 3, beginning near 5862 and 6493, appear to be too great to be wholly accounted for by the titanium oxide flutings which occur in these parts of the spectrum. This is especially the case with the band at 5862, which is very frequently a wide and dark band in the stars, whereas the fluting at 5863·5 is an inconspicuous feature of the titanium oxide spectrum. The flutings in the neighbourhood of 6493 also seem to be too feebly marked in the titanium spectrum to produce a conspicuous absorption head in the stars. More accurate wave-lengths of the stellar bands in question are urgently required for further investigations of their origin.

FLUTED SPECTRUM OF TITANIUM OXIDE.

(ARC-FLAME SPECTRUM OF TiO_2, 1–4, ON IRON POLES, 5, ON CARBON POLES)
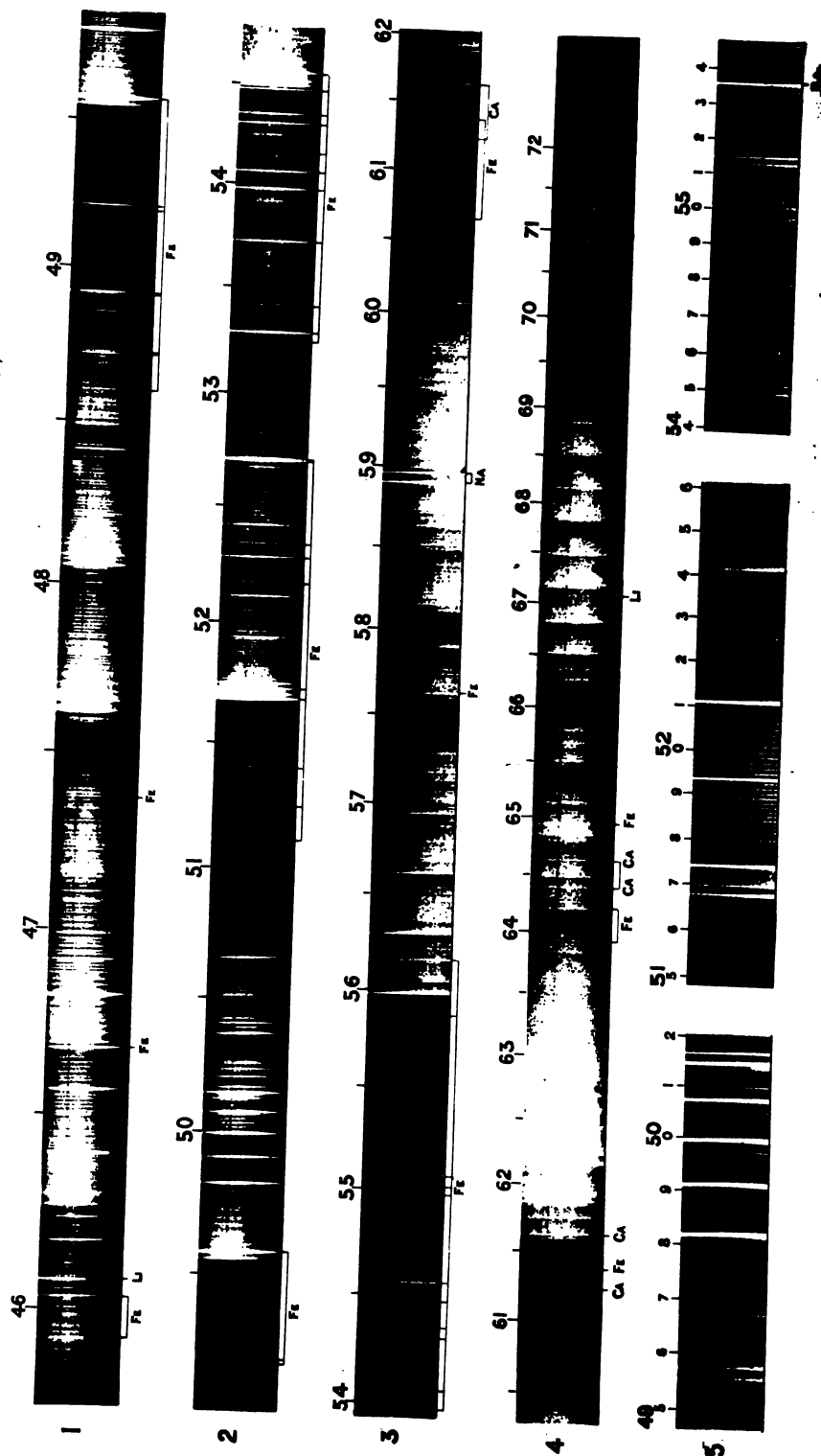
The Osmotic Pressure of Compressible Solutions of any Degree of Concentration.

By Alfred W. Porter, B.Sc., Fellow of, and Assistant-Professor of Physics in, University College, London.

This paper is an attempt to make more complete the theory of solutions, at the same time maintaining as great simplicity of treatment as is possible without sacrificing precision. Renewed attention has been called to the subject, owing to the success of the experiments of the Earl of Berkeley and Mr. E. J. Hartley on the osmotic pressure of concentrated solutions of sugars. Diversity of opinion has existed in regard to the interpretation of these experiments, insufficient attention having been previously paid to the influence of the hydrostatic pressure of the pure solvent upon the value of the osmotic pressure. The principal advances made in this paper consist in simply demonstrating the influence of pressure upon osmotic pressure for *compressible* solutions and in including the effect of the variability of vapour pressure with hydrostatic pressure. The influences of accidental properties (such as the effects of gravitation) are excluded.

Summary of Notation.

The following is the notation employed. All the values are isothermal values.

Solution.—

Hydrostatic pressure	p
Vapour pressure corresponding to hydrostatic pressure p	π_p
„ „ when solution is in contact with its own vapour alone	π_π
Volume at hydrostatic pressure p	V_p
Reduction of volume when 1 gramme of solvent escapes	s_p
Osmotic pressure for hydrostatic pressure p	P_p
„ „ π_π	P_π

Solvent.—

Pressure of solvent when solution is at pressure p	p_0
Corresponding vapour pressure	$\pi_{0_{p_0}}$
Vapour pressure when hydrostatic pressure is that of its own vapour	π_{00}

Volume at hydrostatic pressure p_0 .... $V_{0_{p_0}}$

„   „   „ π_{00}................................. $V_{0_{\pi_0}}$

Specific volume at hydrostatic pressure p_0....................... u_{p_0}

„   „   „   „ π_{00} .... u_{π_0}

Vapour of Solvent.—

Specific volume at pressure π_{00} .... v_0

„   „ π_{p_0} .... v_{p_0}

„   „ π_p .... v_{π_p}

A few special symbols are defined in the text.

Relation between Osmotic and Vapour Pressures.

The following isothermal cycle enables the above relation to be found.   A large (practically infinite) quantity of a solution (unacted upon by any bodily field of force, such as gravity) is separated from a quantity of pure solvent by a semi-permeable membrane.   The solute is supposed to be involatile.   The solution is under a hydrostatic pressure p, while the solvent is under the hydrostatic pressure p_0 for which there will be equilibrium.   It is not intended that either of these pressures shall be restricted to be the vapour pressure of the corresponding liquid.
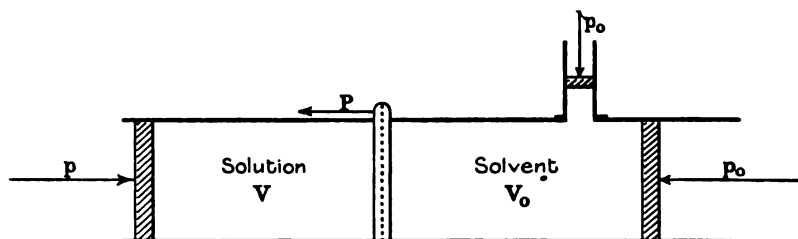
Fig. 1.

(1) Transfer 1 gramme of solvent from the solution to the solvent by moving the semi-permeable membrane to the left; the work done upon the system is

$$P_p s_p - p_0 (u_{p_0} - s_p).$$

(2) Separate 1 gramme of the pure solvent (at p_0) from the rest by partitioning off the lateral tube; change its pressure to π_{00} (by aid of the lateral piston), so that it will be in equilibrium with its own vapour, and then evaporate it; the work done is

$$-\int_{u_{p_0}}^{u_{\pi_0}} p\,du - \pi_{00}(v_0 - u_{\pi_0}).$$

(3) Change the pressure of the vapour to π_π, so that it may be in

equilibrium with the solution when under the hydrostatic pressure of its vapour alone ; the work done is

$$-\int_{\pi_{00}}^{\pi_\pi} p dv.$$

(4) Close the semi-permeable membrane by a shutter to which hydrostatic pressure p_0 can be applied; also enclose the solution by a second shutter, to which a pressure p may be applied; the solution may now be removed. Change its pressure to π_π, bring it into contact with the separated vapour of the solvent, which is also at a pressure π_π; condense this vapour into it, thereby increasing the volume of the solution by s_π, and then compress to a pressure p. The work done is

$$-\int_{p}^{\pi_\pi} p d\mathrm{V} + \pi_\pi (v_\pi - s_\pi) + \int_{p}^{\pi_\pi} p d(\mathrm{V} + s).$$

The connection through the semi-permeable membrane must now be restored, and then everything will be in its initial state, and the total work done, since the cycle is isothermal, must be zero.

Adding the several terms, integrating by parts, and simplifying this equation, we obtain

$$(\mathrm{P}_p + p_0) s_p - p s_p - \int_{\pi_{00}}^{p_0} u dp - \int_{\pi_\pi}^{\pi_{00}} v dp + \int_{\pi_\pi}^{p} s dp = 0 ;$$

or, remembering that $\mathrm{P}_p = p - p_0$,

$$\int_{\pi_\pi}^{p} s dp = \int_{\pi_\pi}^{\pi_{00}} v dp + \int_{\pi_{00}}^{p-\mathrm{P}_p} u dp. \tag{1}$$

This is the expression which gives the osmotic pressure for any concentration and temperature in terms of the vapour pressures, etc., corresponding to the same concentration and temperature. It includes the influence of compressibility, and states with precision the particular circumstances to which the various physical data correspond. For example, the vapour pressures π_{00} and π_π are the vapour pressures of the solvent and solution *each under the hydrostatic pressure of its own vapour*, and not under the hydrostatic pressures p_0 and p respectively, as might perhaps have been expected.

In order to compare this equation with those hitherto given, we will first assume that s and u are constants (that is, we ignore compressibility), and that the vapour follows the gas laws. The equation then becomes

$$(p - \pi_\pi) s + (\pi_{00} - p_0) u = \mathrm{RT} \log (\pi_{00}/\pi_\pi), \tag{2}$$

where R is the gas constant for solvent vapour. This may also be written

$$(\mathrm{P}_p + p_0 - \pi_\pi) s + (\mathrm{P}_p + \pi_{00} - p) u = \mathrm{RT} \log (\pi_{00}/\pi_\pi). \tag{3}$$

The following special cases are of interest.

1st. Let P_{π_0} be the osmotic pressure when the solvent is under the hydrostatic pressure π_{00} of its own vapour; then

$$(P_{\pi_0} + \pi_{00} - \pi_\pi)\, s = RT \log (\pi_{00}/\pi_\pi). \qquad (4)$$

This is identical with van't Hoff's case, except that he writes it in terms of molecular quantities and pays no attention to the variation of P and π with hydrostatic pressure.

2nd. Let P_π be the osmotic pressure when the *solution* is under the hydrostatic pressure π_π of its own vapour; then

$$(P_\pi + \pi_{00} - \pi_\pi)\, u = RT \log (\pi_{00}/\pi_\pi). \qquad (5)$$

This is identical with the Earl of Berkeley's solution, in which, however, no attention was paid to the influence of pressure. It is precisely the result naturally given by the method he employs when attention is paid to pressure.

Influence of Hydrostatic Pressure of Solution.

By differentiating formula (2) with respect to p, the concentration (c) and, therefore, the value of π_π being maintained constant, we get

$$\left(\frac{dp_0}{dp}\right)_c = \frac{s}{u}, \quad \text{or} \quad \left(\frac{dP}{dp}\right)_c = \frac{u-s}{u}.$$

This does not allow for compression.

By differentiating the accurate expression equation (1), we get

$$\left(\frac{dP_p}{dp}\right)_c = \frac{u_{p_0} - s_p}{u_{p_0}}, \qquad (6)$$

which is of the same form as before, but the terms have now more precise meanings. Similarly, the rate of change of osmotic pressure with change in the hydrostatic pressure of the solvent is given by

$$\left(\frac{dP_p}{dp_0}\right)_c = \frac{u_{p_0} - s_p}{s_p}. \qquad (7)$$

Comparison of Osmotic Pressures of Solutions of different Substances in the same Solvent.

If we have several solutions of different substances in the same solvent, and if the pure solvent against which they are tested osmotically is under the pressure of its own vapour (π_0), then equation (1) shows that in general if the vapour pressures of the solutions have the same values (when measured for a hydrostatic pressure of the solution equal to their own vapour pressure) the osmotic pressures will be different, for the equation defining P is in this case

$$\int_{\pi_\pi}^{p} s\, dp = \int_{\pi_\pi}^{\pi_{00}} v\, dp, \qquad (8)$$

where $p - \pi_{00} = P_{\pi_0}$ and s varies considerably for different solutions.

If, however, the solutions, instead of the solvent, be under the hydrostatic pressures of their own vapours, and if these pressures be equal, then the solutions will have the same osmotic pressure. For equation (1) then becomes

$$\int_{\pi_\pi - P_\pi}^{\pi_\infty} u\, dp = \int_{\pi_\pi}^{\pi_\infty} v\, dp, \tag{9}$$

and both these terms depend only upon the properties of the pure solvent and the pressures in question.

It is easy to show, however, that this two-fold isotony (for vapour and for osmotic pressures) holds for any hydrostatic pressures of the solutions (the same for all), provided that the vapour pressures be measured for the solutions when *under the same hydrostatic pressure*. This can be shown at once by considering the arrangement represented in fig. 2.
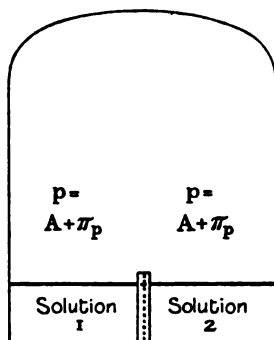
Fig. 2.

Two solutions having the same solvent are contained in a vessel and separated one from the other by a semi-permeable membrane. The space above contains the vapour together with an inert gas whose pressure is A. The vessel is supposed to be in a region free from gravitational action. Then it is obvious that if the osmotic pressures be equal, but the vapour pressures be different, a circulation must ensue which will upset the initial osmotic equilibrium in such a direction as to maintain the difference of vapour pressures and thus to cause perpetual flow; the possibility of this we are entitled to deny.

In order to show how this result is consistent with equation (1), it is necessary to find the mode in which the vapour pressures vary with hydrostatic pressure.

Variation of Vapour Pressure with Hydrostatic Pressure.

An approximate formula for this variation has been obtained by Professor J. J. Thomson in his " Applications of Dynamics to Physics and Chemistry "

by means of the Hamiltonian method. We will proceed to find an exact formula for this variation by means of an isothermal thermodynamic cycle, consisting of several stages :—

A large volume V of solution is taken with a space above containing an inert gas (say, air) and vapour enclosed by a piston semi-permeable to the vapour alone, which is again enclosed by a non-permeable piston. The semi-permeable piston will experience the pressure A due to the inert gas; the pressure on the non-permeable piston will be the pressure of the vapour alone, which is π_p. The volume of the gas and vapour is initially V_A.
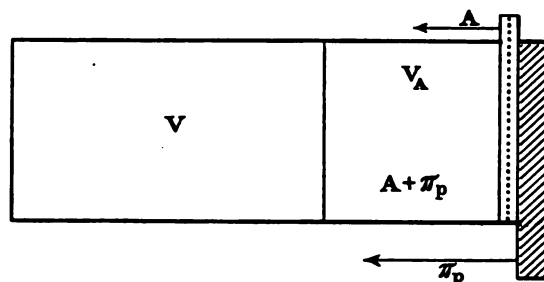
FIG. 3.

(1) Evaporate 1 gramme of solvent from the solution by withdrawing the outer piston, leaving the inner one fixed; work done upon the system in this process is equal to

$$A s_p - \pi_p (v_{\pi_p} - s_p) \quad \text{or} \quad -\pi_p v_{\pi_p} + p s_p,$$

where v_{π_p} is the specific volume of the vapour at the pressure π_p.

(2) Increase the total pressure to $p' = A' + \pi_{p'}$ by moving both pistons such amounts that no further liquid condenses or evaporates. The work done by the inner piston is

$$-\int_{p-\pi_p}^{p'-\pi_{p'}} A \, d \, (V - s + V_A),$$

and that done by the outer piston is

$$-\int_{\pi_p}^{\pi_{p'}} \pi \, d \, (v + V - s + V_A + V_B),$$

where V_B is a volume which represents the fact that the vapour which at the first pressure was to the left of the inner piston may have passed through it on the change of pressure taking place, since the law of compressibility of the vapour will not in general be the same as for the inert gas A.

(3) Condense 1 gramme of the vapour by moving outer piston from right to left, keeping inner piston fixed.

Work done is $\pi_{p'} v_{\pi_{p'}} - p' s_{p'}$.

(4) Restore the original state of the system by suitably moving the two pistons ; work done upon the system is

$$\int_{p-\pi_p}^{p'-\pi_{p'}} A d(V+V_A) + \int_{\pi_p}^{\pi_{p'}} \pi d(V+V_A+V_B),$$

where $\int \pi d V_B$ must be the same as before.

Since the above represents a complete isothermal cycle the total work is zero; that is, after integrating by parts,

$$\int_{p}^{p'} s dp = \int_{\pi_p}^{\pi_{p'}} v dp,$$

whence
$$\partial \pi_p / \partial p = s_p / v_{\pi_p}. \tag{10}$$

It is convenient to take as the upper limits of the two integrals

$$p' = \pi_\pi \quad \text{and} \quad \pi_{p'} = \pi_\pi.$$

This result is for a solution of any concentration; hence, for the pure solvent we have

$$\int_{p_0}^{p_0'} u dp = \int_{\pi_0 p_0}^{\pi_0 p_0'} v dp \quad \text{and} \quad \partial \pi_{0 p_0} / \partial p_0 = u_{p_0} / v_{\pi_0 p_0}. \tag{11}$$

This last result is identical with the result obtained by Professor J. J. Thomson as an approximate solution;[*] we now see that it is accurate, provided that precise meanings be given to the variables concerned.

It is convenient to take as the upper limits of these integrals $p_0' = \pi_{00}$ and $\pi_{0 p_0'} = \pi_{00}$.

By means of these equations we can now transform equation (1).

We have
$$\int_{p}^{\pi_\pi} s dp = \int_{\pi_p}^{\pi_\pi} v dp .$$

Inserting this in (1),

$$\int_{\pi_{00}}^{p-P_p} u dp = \int_{\pi_\pi}^{\pi_p} v dp + \int_{\pi_{00}}^{\pi_\pi} v dp = \int_{\pi_{00}}^{\pi_p} v dp. \tag{12}$$

These integrals depend only upon the properties of the *pure solvent* and upon the limits of integration. If all the limits but one are the same for two solutions under comparison, the remaining limit must also be the same, since the volumes are positive and single-valued functions of the pressures. That is, equality of values of π_p involves equality of the values of P_p, where p is the same for both solutions.[†]

* 'Applications of Dynamics,' p. 171.

† Hence Dr. Larmor's proof (Earl of Berkeley's paper, 'Roy. Soc. Proc.,' A, vol. 79, p. 130) that they have also the same freezing-point can be extended to solutions at any hydrostatic pressure.

The approximate form of the above equation is

$$(P_p - p + \pi_{00})\, u = RT \log(\pi_{00}/\pi_p).$$

When p is the value for which the hydrostatic pressure of the solvent is π_{00}, the left-hand side of this is zero; consequently, in this case $\pi_{00} = \pi_p$ (from the right-hand side). This is simply a special case of a general relation to be proved next.

Again, inserting the value for both $\displaystyle\int_{\pi_\pi}^{p} s\,dp$ and $\displaystyle\int_{\pi_{00}}^{p_0} u\,dp$ into equation (1),

$$\int_{\pi_\pi}^{\pi_p} v\,dp = \int_{\pi_\pi}^{\pi_{00}} v\,dp + \int_{\pi_{00}}^{\pi_0 p_0} v\,dp \quad \text{or} \quad \int_{\pi_0 p_0}^{\pi_p} v\,dp = 0, \quad \text{whence} \quad \pi_p = \pi_{0 p_0}.$$

That is, when a solution is in osmotic equilibrium with the pure solvent, the vapour pressure of the solution is equal to the vapour pressure of the pure solvent, each measured for the actual hydrostatic pressure of the fluid to which it refers.

That this is so is almost immediately evident from the following case:—
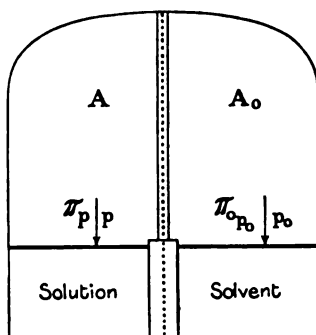
Fig. 4.

The solution and solvent are placed in a vessel and separated by a semi-permeable membrane. The space above is also separated into two parts by a partition semi-permeable to the vapour of the solvent, but not to an inert gas. A pressure difference $p - p_0 = P_p$ is maintained between the two sides by aid of an inert gas. Then, unless the vapour pressures π_p and $\pi_{0 p_0}$ are equal, a flow of vapour will occur with such consequent evaporation and condensation on the two fluids respectively as to upset the initial osmotic equilibrium in a direction which will maintain the difference of vapour pressures and thus cause perpetual flow, the possibility of which we are entitled to deny. This conclusion may be taken as a check upon the equations which we have derived.

We have considered only the case of a non-volatile solute, but it is easy to see that this theorem must be equally true if the solute is volatile; for the

upper partition may be taken impermeable to the vapour of the solute ; and the argument is, in such a case, in no way changed.

Standard Conditions of Measurement.

In whatever experimental ways osmotic pressures may be determined, it is necessary to decide on the standard conditions to which the obtained values shall be reduced for the purposes of tabulation and comparison ; that is, to what hydrostatic pressure shall they refer ? When osmotic pressures are compared by De Vries' original method, as they still often are (by means of vegetable or animal cells), the *solution* is under only a moderate pressure. On the other hand, when values are obtained by the method adopted by the Earl of Berkeley, it is the *pure solvent* that is under a moderate pressure. The values of the osmotic pressure will differ in general in the two cases.

Now it seems most natural to reduce always either to the value corresponding to the solvent under its own vapour alone or to that corresponding to the solution under its own vapour alone ; and of these two, the latter seems the better. It is indeed most natural of all to think of the osmotic pressure as being a property of the solution (just as its vapour pressure, volume, etc., are), the pure solvent being only brought into consideration in a secondary way in connection with an experimental mode of determining the osmotic pressure. It may be objected that if this standard be adopted the equilibrium pressure of the pure solvent will, even for moderate strengths of solution, usually be negative ; that is, the solvent would require to be under tension. The difficulty is relieved when it is remembered that a certain amount of tension in liquids is practically possible, and the osmotic pressure for a strong solution might always be conceived as being measured against a less strong solution, and this in turn against a less, and so on, till the pure solvent was reached. If this standard be adopted, we have, from equation (1),

$$\int_{\pi_\pi - P_\pi}^{\pi_\infty} u\,dp = \int_{\pi_\pi}^{\pi_\infty} v\,dp,$$

an equation which is capable of being graphically represented on the indicator diagram for the pure solvent (fig. 5).

The equation, in fact, states that the hatched area must be taken equal to the dotted area ; the vertical height of the former then gives the osmotic pressure.

Summary of Results.

The chief results obtained in this paper are :—

1. An exact equation is obtained connecting the osmotic pressure and vapour pressure for a solution of any given concentration, of any degree of

compressibility, and under any hydrostatic pressure. This equation is applicable, therefore, even in the neighbourhood of the critical point.

2. Exact equations are obtained giving the dependence of osmotic pressure and vapour pressure upon hydrostatic pressure.
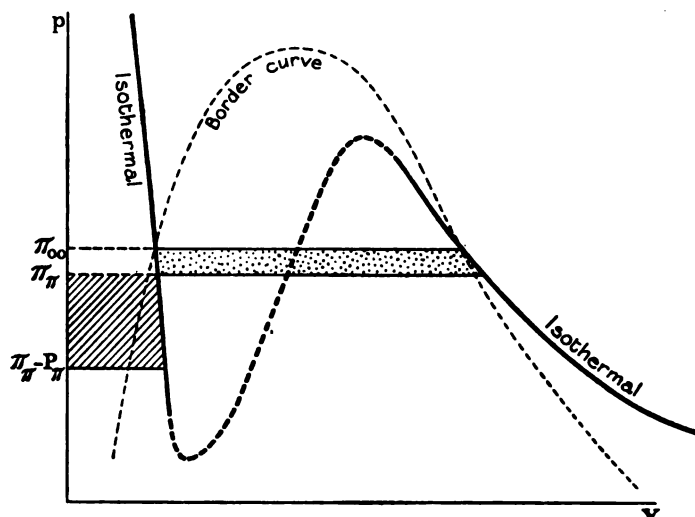
Fig. 5.

3. It is shown that when a solution at any pressure is in equilibrium through a semi-permeable membrane with the pure solvent, its vapour pressure is equal to the vapour pressure of the solvent, *these being measured for the hydrostatic pressures to which the solution and solvent are respectively subjected.*

4. It is shown that if two solutions, *at any hydrostatic pressure the same for both*, are isotonic as regards vapour pressure, they are also isotonic as regards osmotic pressure and they have the same freezing point.

Note on the Use of the Radiometer in Observing Small Gas Pressures; Application to the Detection of the Gaseous Products produced by Radio-active Bodies.

By Sir James Dewar, M.A., Sc.D., LL.D., F.R.S.

Some time ago I exhibited at a soirée of the Royal Society a few experiments with the Crookes radiometer, the object being to show that when helium is the residuary gas filling the instrument, an attached charcoal condenser, even when placed in liquid hydrogen, is unable to diminish the pressure by absorption to such an extent that the radiometer will not rotate (when subjected to the concentrated beam of an electric arc lamp focussed upon the black surface of the mica vanes); while, on the other hand, if the gas instead of being helium is hydrogen, all radiometer motion is suspended. Even when the charcoal condenser of the helium radiometer was cooled in solid hydrogen under exhaustion so that a temperature of 15° absolute was reached, the rotation of the instrument was still very marked. If the radiometer is repeatedly washed out with the mixed oxygen and nitrogen got from the evaporation of liquid air, the charcoal and the whole of the glass being thoroughly heated and the apparatus finally exhausted to a fraction of a millimetre and sealed off, then, on placing the charcoal tube in liquid air, generally after an hour or two the vacuum is so high that no motion is induced by the beam of the electric arc. But if instead of liquid air the cooling agent is liquid hydrogen, then two minutes' immersion is sufficient to effect the same result, provided the radiometer is small and the gases get down a quill tube direct into the charcoal. Instead of the gases from liquid air being used to clean out the radiometer as described, it is for some purposes better to seal on a side tube containing perchlorate of potassium, which, when heated, gives pure oxygen. Further, in many experiments it is advantageous to exhaust the radiometer with its little charcoal condenser by means of a larger quantity of charcoal placed in liquid air for a night and then to seal the latter off before cooling the special charcoal bulb attached to the radiometer. When a McLeod gauge was sealed on to the end of the bulb containing the charcoal condenser which is cooled in liquid air (no stop-cocks of any kind being used), all the mercury vapour was eliminated from the radiometer, and the pressure of the permanent gas was found to be 0·00001 mm., or one seventy-six millionth of an atmosphere. In this condition the radiometer moved when the image of the poles was focussed on the black

vanes and after some 15 minutes' heating the pressure was found to be only one twenty-five millionth of an atmosphere and the pressure remained at this after 10 hours' cooling of the charcoal condenser in liquid air. The gas produced was no doubt hydrogen, got from the lamp black of the mica vanes, this being the first time the instrument was used. As a rule the radiometers require to be refilled, exhausted and tested more than once in order to get the motion reduced to a minimum. The importance of the removal of traces of gases like helium, hydrogen or neon is shown from the fact that a radiometer which has the charcoal removed from the attached bulb, and the latter cooled in liquid hydrogen (the instrument having been previously filled with dry air and exhausted to a fraction of a millimetre of mercury), will not reach such a vacuum as to stop the radiometer motion. Now, as the pressure of nitrogen at the boiling point of hydrogen must be of the order of a millionth of a millionth of an atmosphere, the action must come either from uncondensable gases, or the persistent adhesion of gas molecules to the glass and vanes of the radiometer or to some solid matter volatile under the conditions of the experiment. The lowest pressure reached in a charcoal vacuum after 10 minutes' cooling in solid hydrogen was still one hundred millionth of an atmosphere. The pressure observed is thus far too high and it may be that some of this is due to hydrogen coming from the charcoal. To get really high vacua by the charcoal method, even when liquid hydrogen is the cooling agent, it seems necessary to allow the absorption to go on for an hour or more, when the space to be exhausted is relatively large, and where narrow tubes or orifices constitute part of the apparatus, as in the McLeod gauge. Further, the presence of any organic matter on the vanes is fatal. No amount of cooling of the charcoal in liquid hydrogen of a radiometer filled as usual and tested in the ordinary manner, in which the vanes were made of pith, makes a vacuum sufficient to stop the radiometer motion. The concentrated beam, each time it was applied, was generating gas. In all the experiments the arc used was expending 10 ampères and the focus was adjusted to about 3 feet from the lamp. The radiometers had a volume of from 150 to 20 c.c.

Finding the McLeod gauge very difficult to use, a new method of defining the maximum limit of the working pressure (under the defined circumstances) depending upon the vapour-pressure of mercury was devised. For this purpose a side tube was sealed on to the top of the radiometer and this, after being bent twice at right angles, ended in a little bulb containing a globule of mercury. After the radiometer and charcoal were heated and exhausted and repeatedly washed out with the gas from liquid air, the charcoal was cooled in liquid air and the mercury allowed to

distil for an hour or two. After this treatment, on cooling the mercury with liquid air, the radiometer in a short time became inactive. In this condition the mercury was placed in an alcohol bath at −80° C. and the temperature allowed to rise slowly.

In this way it was found the radiometer action began in the instrument used at −23° C. The pressure of mercury vapour for the temperature derived from the Hertz formulæ is found to be about a fifty millionth of an atmosphere. All the time of the experiment the mercury vapour was being sucked out of the radiometer by the liquid air cooling of the charcoal tube, so that the pressure might be less than the saturated pressure. This result at once suggested that the method ought to be applicable to the detection of the gaseous products derived from the transformation of radio-active bodies. In order to test this application, a side tube containing a little radium bromide was sealed on to the bottom of the charcoal condenser, in order to remove the emanation by absorption in the charcoal kept in liquid air. The radiometer, after thorough washing with the gas from liquid air, heating and exhaustion by a subsidiary charcoal condenser placed in liquid air that was sealed off, was found inactive after the small charcoal receptacle was cooled for an hour in liquid air. The radiometer was again tested after standing 15 hours and was found to be quite active. It would seem that the gas produced must be hydrogen, helium, or the alpha particles. In order to eliminate any hydrogen that might be produced, the charcoal condenser of the radiometer was transferred from liquid air, in which it had been kept for some two days, into liquid hydrogen. After half an hour's cooling the motion was active when the image of the arc lamp was focussed on the black surface of the mica vanes of the radiometer, and even after one hour's immersion of the charcoal in the liquid hydrogen the motion suffered no diminution. The active gas must, therefore, have been helium along with it may be the alpha particles ; unless one is being deceived by some solid deposited on the radiometer vanes sufficiently volatile when the arc light is concentrated on them to cause the motion. A similar radiometer to that which was used in the radium experiment had a side tube attached containing some 50 grammes of thoria, and after the usual treatment was found inactive. After keeping a fortnight it is now active, but I have not had the opportunity of cooling the charcoal in liquid hydrogen, so that the possibility of the gas being hydrogen has not been eliminated. We might anticipate that monadic gases of the type of helium and mercury would be more effective than the ordinary gases in inducing radiometer motion. A radiometer with a helium residue will still work under fixed conditions when the gas pressure is four or five times higher than one containing an oxygen residuum. Again, the sensibility of the

instrument ought to increase, provided it was subjected to the same intensity of radiation while immersed in liquid air or liquid hydrogen.

The experiments, in any case, seem to show that the radiometer may be used as an efficient instrument of research for the detection of small gas pressures and the study of radio-active products. For quantitative measurements the torsion balance or bifilar suspension must be employed. It would be interesting to repeat light repulsion experiments in the highest attainable charcoal vacuum. Later on I hope to extend the investigation.

Some Notes on Carbon at High Temperatures and Pressures.

By Hon. C. A. PARSONS, C.B., Sc.D., F.R.S.

Following the subject of my paper of 1888 to this Society, which will be referred to in a subsequent communication, attempts have recently been made to melt carbon by electrical resistance heating under pressure, and the following is a short summary of the results of about 100 experiments.

The procedure has been on two lines. In the first, carbon is treated in bulk in a thick tube of 8 inches internal diameter of gun steel closed below by a massive pole of steel insulated from but gas tight with the mould and above by a closely fitting steel ram packed by copper rings imbedded in grooves in the ram or by leather and steel cups according to whether solids, liquids or gases are to be contained. The bore of the mould is generally lined with asbestos and after being charged the whole is placed under a 2000-ton press, the head and baseplate being insulated and connected to the terminals of a 300-kilowatt storage battery with coupling arrangements for 4, 8, 16 or 48 volts.

It was hoped that the greater thermal and electrical conductivity of steel as compared with carbon or graphite at moderate temperatures would with the help of water jackets keep the outer layers comparatively cool and that the increased conductivity of the central portions consequent on their higher temperature and conversion to graphite would so centralise the current on the core lying between the poles as to melt it.

Further concentration of current was obtained in the initial stages of heating by packing the central portion with carbon rods on end or by a compressed graphite core, and filling in around with coarsely broken arc-light carbon, or with wood charcoal (which is a bad conductor until highly heated).

With pressures of about 30 tons per square inch, and currents commencing

at 6000 ampères, increasing up to 50,000 ampères, with about 2 volts between the terminals of the mould, the carbon rods were partially converted to graphite and firmly welded together; in the case of the graphite core the flakes were much increased in size.

The heating was in all cases limited by the melting of the steel poles and resulted in short circuits in the mould from the permeation of the asbestos by the molten iron. Neither the internal water-jacketing of the poles nor the substitution of copper poles for steel have remedied this trouble.

It appears that the thermal conductivity of the carbon or graphite at or near the temperature of vaporisation is very greatly in excess of that anticipated, or that the rapid transfer of heat is caused by carbon vapour, which appears to have a great power of penetration through carbon at high temperatures. The melting of the poles and the destruction caused by short circuits which reached 80,000 ampères in the mould were not only costly to remedy, but caused contamination of the carbon from the metal of the poles and the insulating material.

In several experiments a nucleus of very soft graphite about $2\frac{1}{2}$ inches in diameter was found in the centre. And in several experiments small masses of iron, highly charged with graphite, were found in varying positions among the carbon or graphite.

This method, however, would probably be more successful if carried out on a much larger scale, as for a given central temperature the transfer of heat to the poles and mould would be less, and water-jackets would then prove more effective. It is, however, difficult to construct water-jackets to withstand more than 30 tons per square inch, and unless made of hard steel they crush in. The maximum power of the press is 2500 tons, and with the apparatus at hand if the size of the mould was much increased the pressure in the mould would have to be decreased.

Another plan was then adopted of interposing an insulating barrier of some refractory material with a hole in it between the poles, the charge in the first instance being graphite. It was hoped that by means of electrical currents of higher potential and large volume the energy would be so concentrated on the small volume in the neck as to melt it before it had time to form carbides with the material of the barrier.

This was to some extent achieved in that the graphite in the centre was converted to a softer and more flaky nature.

In one of these experiments the barrier was formed out of a block of fused magnesium oxide, specific gravity 3·65, and the pressure in the mould, which was 4 inches in internal diameter, was in this case raised to 100 tons per square inch. The strongest steel poles were required for this pressure

also the mould of gun steel became permanently strained and required reboring after each experiment.

A current at about 12 volts at the terminals in the mould, developing about 100 kilowatts, was turned on for seven seconds.

The initial diameter of the hole in the barrier was $\frac{5}{8}$ inch and the thickness about $\frac{3}{4}$ inch.* This barrier was converted to magnesium carbide of a green colour to a radial depth of about $\frac{3}{8}$ inch. Thus this magnesium oxide when heated under pressure with graphite readily forms a carbide. The graphite in the centre was altered to large and very soft flakes. Neither the graphite nor the magnesium carbide contained any hard crystalline carbon.

Similar experiments were tried with carbon rods surrounded by silica, and as a guide to the temperature reached, current was turned on of just sufficient voltage to convert the rod to graphite; the mould was then set up afresh and double the voltage applied, when the rod was vaporised and disseminated throughout the molten silica, principally in the form of graphite of very small grain, very little silicon and still less silicide of carbon being formed.

Another series of experiments have been made to investigate the behaviour of vaporised carbon under fluid or gaseous pressures of about 30 tons per square inch. The general arrangement of the mould consisted of a central carbon rod with a lining of marble; in some cases the space between the rod and marble was packed with coarsely powdered charcoal.

Several compounds of carbon were treated, perhaps the most interesting being carbon dioxide. The liquid was run into the mould and a pressure of 30 tons per square inch applied. It was found that its volume diminished to about 80 per cent., due to its compressibility. Current was then passed through the rod, and the liquid must then have existed as gaseous carbon monoxide in the hotter zones.

When cooled, the liquid and gas were allowed to escape; a sample of this gas on analysis was found to contain 95 per cent. of carbon monoxide and 3 per cent. carbon dioxide, the residue consisting apparently of nitrogen.

As the pressure of 30 tons was maintained throughout the experiment, it would seem that the compressibility of carbon monoxide diminishes rapidly at such high pressures, but this experiment will be repeated and will form the subject of a subsequent paper on the compressibility of liquids and gases. Part of the central carbon was converted to graphite, and in one place there was found a nest of woolly deposited carbon, showing that under a pressure of 30 tons per square inch carbon vaporised in carbon monoxide is deposited in the form of amorphous carbon.

* The heat units delivered on to the neck being about four times that required to raise the graphite column through 5000° C., taking the specific heat at 0·5.

Conclusions.

From these experiments several hundred samples have been carefully analysed. In none of the experiments designed to melt or vaporise carbon under pressure has the residue contained more than a suspicion of black or transparent diamond.

In no experiment we have made has there been any sign of the carbon becoming a non-conductor, and the impression derived is undoubtedly that soft crystals of graphite are the resulting stable form of carbon after heating to very high temperatures.

At very high temperatures and pressures graphite has a great tendency to permeate or diffuse into its cooler surroundings. It should, however, be noted that in all the experiments so far made it has been found impossible to exclude from the graphite other substances in the liquid or gaseous state.

Though in many of the foregoing experiments the molten steel of the poles became highly charged with graphite, further experiments have been made to ascertain the influence of pressure upon iron highly charged with carbon. Cores formed of iron rods, iron tubes filled with carbon or with various proportions of iron filings and lamp black, surrounded with various substances such as charcoal, magnesia, olivine, etc., were melted or vaporised and disseminated throughout the charge.

Thus iron highly charged with carbon under a pressure of 30 to 50 tons was cooled at various rates according to its proximity to the sides of the mould, the analysis showing in most cases no residue at all, but occasionally a suspicion of very minute diamond. As a further experiment, a small carbon crucible containing iron highly charged with carbon from the electric furnace was quickly transferred to a steel die and subjected, while still far above the melting point, to a pressure of 75 tons per square inch.

The analysis showed scarcely any crystalline residue and probably less than if the crucible had been cooled in water at atmospheric pressure, and as it would seem that 75 tons or even 30 tons per square inch must be a greater pressure than can be produced in the interior of a spheroidal mass of cast iron when suddenly cooled, the inference from these experiments seems to be that mechanical pressure is not the cause of the production of diamond in rapidly cooled iron.

We hope to be able to communicate further experiments on this subject during the course of next session.

I would wish to add that most of the analyses have been made by Mr. J. Trevor Cart.

Ranges and Behaviour of Rifled Projectiles in Air.

By A. Mallock, F.R.S.

In a former paper it was shown that the distance which a pointed projectile* would travel in air, when air resistance was the only force acting on it, could be very closely expressed by the formula $s = v't + \frac{u_0}{a}(1 - e^{-at})$. In the present paper I propose to examine the nature of the motion of such a projectile when gravity acts on it, as well as air resistance.

Suppose that projectile is started at an angle a with the horizon. Without the action of gravity at the end of time t, the projectile will have attained a height of $s \sin a$ above the surface of the ground. It is easy to see (the proof, however, is given in the notes) that, if gravity acts and is the only force which has a component normal to the trajectory, the position of the projectile at t will, if x and y are the horizontal and vertical co-ordinates, be $x = s \cos a$, $y = s \sin a - \frac{1}{2} gt^2$. Thus if we put $y = 0$, i.e., if the projectile reaches the ground after time t, the range for an elevation a is $s = \frac{1}{2} gt^2 / \sin a$, so that $\sin a = gt^2 / 2s$. Experiment, however, shows that this relation does not hold, and it must be concluded, therefore, that gravity is not the only force acting which has a component normal to the trajectory.

Experiment also shows that the axis of an elongated rifled projectile tends to set itself in the direction of the tangent to the trajectory, and it will appear that the small angle between the axis and the tangent is the origin of the normal force which causes the simple relation $\sin a = gt^2 / 2s$ to fail; the fact being that the long projectile with its axis slightly inclined to the direction of motion behaves as a rather imperfect sort of flying machine, the upward component of the resistance on the underside of the shot acting to diminish the effect of gravity.

That this was so was well known to the late W. E. Metford, who did so much for the improvement of small arms; but I cannot find that it has been taken into account by artillerists, nor, as far as I know, has any dynamical explanation of the tendency of the axis of a rifled shot to follow the direction of the tangent to the trajectory been published, though part, at any rate, of the true reason was given in conversation by the late W. Froude more than 30 years ago.

* The projectile here referred to is ogival-headed, the radius of the ogive being two diameters.

We know that if a rifled shot were fired *in vacuo* its axis of rotation would remain parallel to its initial position throughout its flight. In order to examine the reason why the same shot fired in air should keep its axis of rotation nearly parallel to the tangent of the trajectory, it will be convenient to take at first a simpler case.

Imagine a top or gyrostat of any shape (any surface of revolution) supported in gymbals and placed at one end of a long arm, in a vertical plane, the other end of the arm being fixed to a horizontal axis (see fig. 1).

Fɪɢ. 1.

If the gyrostat be set spinning, and the arm is then made to rotate about its horizontal axis, we know that, in the absence of any external force, the axis of the gyroscope will always remain parallel to the position it occupied when first set spinning.

Suppose this direction to be the tangent to the circle described by the C.G. of the shot about the horizontal axis AB, I will first inquire what the magnitude and direction of the couple must be which will cause the axis of the shot to remain tangential to the circle when the arm revolves at a definite angular speed.

The mathematical expressions for the required couple are given in the notes.

It appears (*a*) that the axis of the requisite couple is parallel to the arm R ; (*b*) that it must tend to cause rotation in the same direction as the projectile would be spinning if the head of the latter was pointing towards the axis AB ;

(c) that its magnitude is directly proportional to the angular speed of the arm about AB and to the angular speed of the gyrostat about its axis; and (d) to the fourth power of the linear dimensions of the projectile.

If, now, in imagination, we make the arm R equal in length to the radius of curvature of the trajectory of a projectile and the angular speed of the arm such that its end has the speed of the projectile, and give the gyrostat the spin which would be given by the rifling, we know that, in some way or other, the air must call into action a couple with the above specified direction and magnitude.

As a numerical example showing the order of magnitude of the required couple, I give the following figures relating to a 12-inch, 6-inch, and 0·303-inch projectile. The couple which must act about the radius of curvature of the trajectory through the C.G. of a projectile having a velocity of 2000 f.s. and making one whole turn about its axis while it travels 30 diameters is:—

> 12-inch gun .... 11·15 ft.-lbs.
> 6-inch gun .... 0·66 „
> 0·303-inch rifle ...... $1·02 \times 10^{-5}$ ft.-lb. = about 8·6-inch grains.

The action of the air in producing this couple may best be illustrated by the action of a jet of water on a rotating body. It is evident that if the axis of the jet and the axis of rotation are identical, the rotation communicated to the fluid by friction, as it spreads over the surface of the body after impact, will be symmetrical about the axis, and the speed of rotation of the projectile will, therefore, unless maintained from without, gradually decrease, but beyond this there will be no effect. The case is different, however, if the axes of the jet and of rotation are inclined.

Suppose in the first place that these two axes intersect at a point in the projectile (which may be called the centre of pressure) independent of the angle (provided the angle remains small), and that the mass in the projectile is so distributed fore and aft as to make this point the centre of gravity. In this condition the jet, although it impinges obliquely on the projectile, exerts no couple in the plane containing the two axes.

There is a couple, however, acting in a plane through the jet perpendicular to the plane containing the axis of the jet and the axis of rotation; for the jet impinges on the surface of the projectile at some distance from the axis of rotation. Surface friction therefore imparts sideways velocity to the jet after impact. Thus the reaction constitutes a force urging the surface of the projectile, at the point of impact, in a direction opposite to that in which the surface is moving, and this force can be calculated. If the effect on

impact were the only action of the jet, the force just mentioned, together with the inertia of the shot, would constitute a couple acting in the direction required to bring the axis of rotation towards the axis of the jet.[*]   As a matter of fact, however, the fluid in leaving the surface of the projectile also exercises a force there, the resultant of which is in the opposite direction to that called up by the impact of the jet.

The magnitude of this force cannot at present be calculated from dynamical principles, but can be shown to exist by experiment, and by appropriate experiments could be measured.

Its origin can be explained thus : Suppose a cylinder immersed in a current of fluid with its axis at right angles to the stream.   If the fluid were the perfect fluid of mathematicians, the stream lines would flow in behind the cylinder in curves precisely similar to those they followed while approaching it.

A real fluid, such as air or water, does not behave in this way.   In approaching the solid the stream lines conform nearly to the theoretical flow of a perfect fluid, but, instead of closing in behind, the streams leave the solid surface altogether near its greatest diameter, and enclose between them a body of fluid constituting a wake.   The motion of the fluid in the wake is of a very complicated character, consisting of eddies which are always being formed in the immediate neighbourhood of the solid, and breaking away from it when they have reached a certain size.

The angle which the average of the wake makes with the direction of flow is unstable within certain limits, so that the wake tends to trail away from the solid at some small angle to the general direction of the stream, implying a lateral force on the solid.

If the cylinder is stationary, the direction which the instability takes varies quickly, and, looking back along the wake for some distance, its mean direction will appear to be that of the stream, but its course will be sinuous, owing to the successive changes in the direction of instability.   If, however, the cylinder is made to revolve, the direction of the instability is settled, and the wake leaves with a sideways component of velocity in the direction of the motion of the rear surface of the cylinder.

Even a slow rotation of the cylinder (*i.e.*, a rotation giving a surface velocity less than the velocity of the stream) suffices to give the wake a considerable lateral deviation ; but the angle between the wake and the stream increases with the velocity of rotation of the cylinder, though in what proportion I do not at present know (the curious flight of a golf ball with underspin depends on the action just described).

[*] This was the explanation given by W. Froude.

The cylinder has hitherto been supposed to have its axis at right angles to the direction of flow, but now let it be gradually turned so as to bring the axis of rotation towards the direction of the stream. When the two are nearly coincident the greater part of the wake, of course, belongs to the base of the cylinder, but part still belongs to that part of the side which is, as it were, in shadow; and as long as any shadowed part remains, some of the wake leaves with a sideways velocity having the direction of the surface motion of the shadowed part. This necessarily implies a force on the cylinder in the opposite direction.

What the angle between the axis of the projectile and its direction of motion is at which the shadow vanishes, I have not determined. It is certainly small, and varies with the shape of the head; with flat heads it is probably less than a degree.

The statements above depend only on experiments and observations I myself have made. I have no doubt about the existence of the forces, but cannot give their magnitude.

We are left, however, with the fact that a projectile rotating in air, with its axis nearly in the direction of motion, experiences a force in opposite directions at either end which together constitute: (a) a couple tending to bring the axis of rotation towards the direction of motion, and (b) a force (equal to the difference of the forces at the head and tail) tending to move the projectile bodily sideways.* This force is one element of drift.

So far I have supposed that the C.G. of the projectile was at the centre of pressure. In all real projectiles, however, the centre of pressure is, in general, some way in front of the C.G., and, as has often been pointed out, this produces a couple in the plane containing the axis of rotation and the tangent to the trajectory whose magnitude is proportional to the angle between the two, and to the distance between the centre of pressure and the centre of gravity, that is to OC by OCA (fig. 2).

The effect of this couple on the spinning projectile is to cause its axis to describe a cone round the direction of the motion. The time, T, required for the axis to make one complete turn about the direction of motion (the precessional period) is given in the notes.

The air resistance also gives rise to a force tending to move the projectile bodily sideways (in the plane containing the axis of rotation and the direction of motion) which is directly proportional to the angle between them and to the resistance. (The horizontal component of this force is the other element of drift.)

* If the views here expressed are correct, the axis of rotation of a spherical rifled shot should tend to follow the tangent to the trajectory.
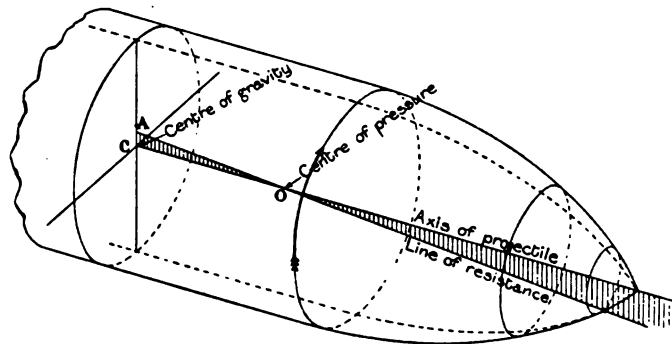
Fig. 2.

Now consider the trace of the axis of the projectile on a plane XOY (fig. 3), at right angles to the direction of motion, the plane having the same speed as the projectile, and O being the point where the tangent to the trajectory meets the plane.
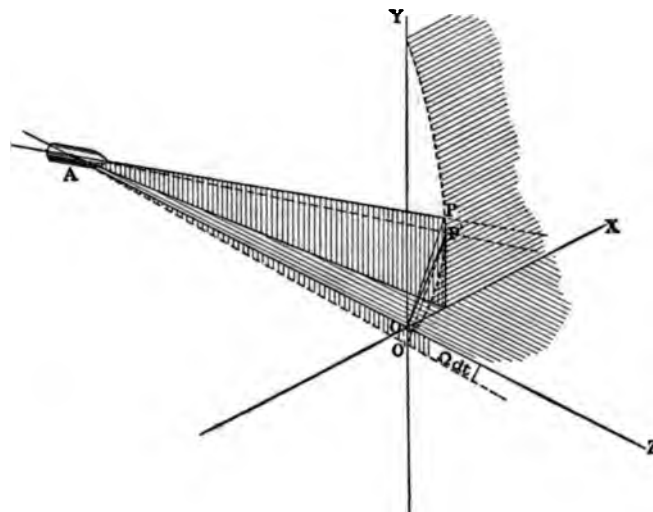
Fig. 3.

In virtue of the couple in the plane OAP($=C_1$), P would describe a circle about O with a velocity proportional to PO.

In virtue of the couple in the plane through Z at right angles to OAP ($=C_2$), P would describe the straight line PO with a velocity also proportional to PO. The combination of the two movements makes the trace of P into an equiangular spiral.

In a real trajectory the direction of the tangent is always changing.

Let O O′ (fig. 3) be the distance which the tangent would trace in time dt

on the plane XOY in virtue of the curvature of the trajectory (O O' of course $= OA . \Omega dt$). If the point P is now on the equiangular spiral at a position where the tangent to the spiral is parallel to the radius of curvature of the trajectory, the element P P' of the spiral is equal to $2\pi T^{-1} OA . \sin \psi \cos \delta$, where $\psi = OAP$, $\delta = $ constant angle of spiral, and T = precessional period, and if $2\pi T^{-1} \sin \psi \cos \delta = \Omega$, ψ is independent of time, the axis of the shot in virtue of its precessional and inward motion changing its position at the same rate as the direction of the tangent to the trajectory.

With a well-formed shot the angle POY is small,* and this proves that the motion due to the couple C_2 (which may be called the extinctive couple, from the analogy of its effect with the effect of resistance to the motion of a conical pendulum) is large compared to the couple C_1.

If we take the algebraic sum of the horizontal and vertical components of the force at the C.G. of the projectile, the first produces drift and the second acts to diminish the effective force of gravity.

It appears, then, that the complete effect of the air resistance on the shot is to produce, in addition to the general retardation of its velocity, two couples: one in the plane containing the axis of the projectile and the tangent to the trajectory, and one in the plane through the tangent at right angles to the first plane; also two forces both normal to the direction of motion, parallel and perpendicular to the radius of curvature of the trajectory.

The reduction in the apparent force of gravity is very considerable and increases with the curvature of the trajectory, that is as the velocity of the projectile diminishes. The relation found between the lifting force and the apparent force of gravity is given in the notes, and is also shown in the diagram, fig. 4.

The meaning attached to "apparent value of gravity" in this paper is defined by the relation

$$\iint (g - f)\, dt = \tfrac{1}{2} g' t^2,$$

where f is the lifting component due to the obliquity of the axis of the shot and direction of its travel and g' is the "apparent value of gravity." In other words, g' is the uniform acceleration which, acting for a time t on a projectile started at an angle to the horizon for which the range is R, causes the projectile to fall through a distance $s \sin \alpha$. In diagram 4 the values of g' are the result of the analysis of a large number of range tables collected during many years. These tables, which refer to nearly all the calibres of rifled guns which have been in use, are based, for the most part, on the ballistic theories given in the text-books, but corrected by the use of

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* If this were not so, the drift would be greater than it is.

suitable multipliers to make them agree with practice. It is clear from the diagram that the value of g' is fairly well expressed by the equation $g' = g - \dfrac{c}{v_0}(v_0 - v)$. For the purpose of finding a general formula for ranges this is all we require, and subject to the condition that the angle α is small enough for $\cos \alpha$ to be taken as unity, we can at once write:—

$$R = v't + \frac{u_0}{a}(1 - e^{-at}).\quad \text{(A)}$$

$$a = \left(g - \frac{c}{u_0}(v_0 - v)\right)\frac{C^2}{2R}.\quad \text{(B)}$$

In the actual construction of range tables it is often convenient to plot R and a in terms of t and then take the simultaneous values, thus getting R in terms of a. There can be no doubt that these formulæ give the ranges with great accuracy when α is small, but a reference to the examples given at the end of this paper shows that even when α is as large as $10°$, that is when $\cos \alpha$ differs from unity by nearly 2 per cent., the agreement is still very close.

The reason for this is that the difference between $\cos \alpha$ and unity, which should be taken into account in the range as given by equation (A) (in which the air is treated as being of constant density), is of the same sign and (with the larger guns) of nearly the same amount as the increase of range due to the diminished density of the air at the higher parts of the trajectory.

A graphic method of finding the correction for variable atmospheric density is given in the notes.

The object of this paper is to show that although experiments which will determine directly what the action of the air is on an
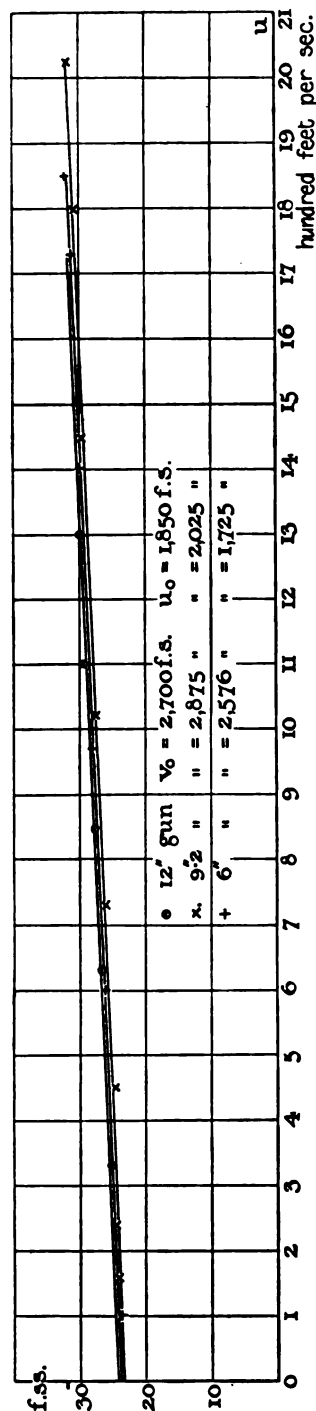
obliquely moving rifled projectile are very desirable, it is possible, neverthe-less, even with existing knowledge to compute with sufficient accuracy the range of any projectile in terms of its initial velocity, weight and diameter, and without the use of any arbitrary constants, except such as are derived from resistance experiments and the constants in the expression for g'.

To be able to do this is an important matter, for it is not such a simple thing as might be supposed to get the true ranges of a large gun by direct experiment.

Range Tables, calculated by Formulæ (A) and (B) for 12-inch Gun, M.V. 2700 f.s.; and 6-inch Gun, M.V. 2575 f.s. Columns III and V give the differences between the Calculated Values and the Values given in the ordinary Range Tables for the same Guns.

12-inch gun.					6-inch gun.				
I. Range.	II. Elevation.	III.	IV. Time of flight.	V.	I. Range.	II. Elevation.	III.	IV. Time of flight.	V.
yds. 0	0 0	0 0	secs. 0·0	0·0	yds. 0	0	0·0	secs. 0·0	0·0
500	11·5	+ 0·5	0·56	+0·00	500	14	+ 1·0	0·62	+0·02
1,000	26·0	+ 2·0	1·2	0·06	1,000	29	+ 2·0	1·22	−0·04
1,500	35·5	− 0·5	1·81	0·07	1,500	44	0·0	1·95	−0·02
2,000	49·0	0·0	2·41	0·07	2,000	1 0	− 1·0	2·72	+0·06
2,500	1 3·5	− 1·0	2·99	0·01	2,500	1 18	− 1·0	3·50	+0·06
3,000	1 17·0	0·0	3·69	0·06	3,000	1 38	− 1·0	4·38	+0·10
3,500	1 31·0	0·0	4·32	0·00	3,500	2 0	0·0	5·26	+0·08
4,000	1 47·0	− 1·0	5·02	0·02	4,000	2 26	+ 2·0	6·20	+0·04
4,500	2 3·0	− 2·0	5·75	0·03	4,500	2 55	+ 1·0	7·20	+0·02
5,000	2 20·0	− 4·0	6·50	0·03	5,000	3 25	+ 1·0	8·35	+0·10
5,500	2 36·0	− 3·0	7·29	0·00	5,500	4 0	0·0	9·55	+0·1
6,000	2 55·0	− 2·0	8·05	0·03	6,000	4 36	+ 4·0	10·75	+0·05
6,500	3 13·0	− 1·0	8·79	−0·1	6,500	5 19	+ 3·0	12·00	+0·03
7,000	3 34·0	0·0	9·67	−0·15	7,000	6 2	+ 3·0	13·40	+0·04
7,500	3 56·0	− 1·0	10·50	−0·02	7,500	6 48	+ 3·0	14·90	+0·10
8,000	4 19·0	0·0	11·38	−0·11	8,000	7 36	0·0	15·80	+0·5
8,500	4 43·0	+ 0·0	12·40	−0·04	8,500	9 8	+37·0	17·50	−0·37
9,000	5 7·0	∓ 1·0	13·42	−0·02	9,000	10 9	+39·0	19·20	−0·29
9,500	5 33·0	− 0·0	14·45	+0·04	9,500	11 10	+42·0	20·95	−0·2
10,000	6 1·0	+ 2·0	15·50	+0·06	10,000	12 12	+32·0	22·8	−0·07
10,500	6 27·0	+ 1·0	16·55	+0·01	10,500	13 13	+21·0	24·65	+0·01
11,000	6 54·0	− 2·0	17·60	+0·01					
11,500	7 22·0	− 4·0	18·65	−0·06					
12,000	7 58·0	− 1·0	19·8	−0·06					
12,500	8 32·0	− 2·0	20·9	−0·14					
13,000	9 14·0	− 9·0	22·2	−0·16					
13,500	9 54·0	−14·0	23·5	−0·17					
14,000	10 39·0	−23·0	24·9	−0·06					
14,500	11 23·0	−30·0	26·25	−0·05					

Computation of Part of Range Table for 12-inch Gun.

W = 850 lb. D = 1 ft. v_0 = 2700 f.s. v_0 = 1850 f.s. v' = 850 f.s. u_0 = 1850 f.s. a = (6·385 D²/W) = 0·784. v_0/a = 24,750 ft.

$c = (8·3/u_0) = 0·0045.$

I. x	II. $t = \frac{x}{a}$	III. e^{-x}	IV. $1-e^{-x}$	V. $v't$	VI. $\frac{u_0}{a}(1-e^{-at})$	VII. S in feet $= v't + \frac{v_0}{a}(1-e^{-at})$	VIII. $u = v_0 e^{-at}$	IX. $v_0 - v$	X. $c(u_0-u)$	XI. $g' = g - c(v_0-v)$	XII. $\frac{g't^2}{2}$	XIII. $\sin \alpha = \frac{g't^2}{2S}$	XIV. α	XV. Range in yards
0·4	5·34	0·6912	0·3288	4520	8,150	12,670	1241	609	2·78	29·47	422·5	0·0382	1° 54	4288
0·5	6·66	0·6090	0·3910	5650	9,680	15,330	1128	722	3·26	28·94	641·5	0·0419	2° 24	5110
0·6	8·00	0·5500	0·4500	6780	11,100	17,880	1019	831	3·75	28·45	924·0	0·0516	2° 58	5960
0·7	9·36	0·4977	0·5023	7910	12,730	20,640	897	953	4·30	27·90	1229·0	0·0595	3° 25	6880
0·8	10·65	0·4505	0·5495	9040	13,580	22,620	834	1016	4·56	27·68	1565·0	0·0699	3° 59	7540

Plotting α in Terms of Range.

Range.	α	Range.	α
4000	1° 46	6000	2° 59
4500	2° 8	6500	3° 15
5000	2° 20	7000	3° 31
5500	2° 39	7500	3° 56

The accidental differences due to a variety of causes between the successive rounds of the same gun make it necessary that a large number of rounds should be fired in order that anything like a true mean should be arrived at, and in the case of large guns such as the 12-inch the alteration in the gun itself (whose life is only about 200 rounds) makes it almost impossible to determine by experiments on a single gun what the true range is when the gun is new. Any formula, therefore, which will give the range with accuracy is not only a matter of convenience, but of economy, both in ammunition and wear of guns.

In the examples given (p. 544) of angles of elevations and ranges computed by equations (A) and (B), the third and fifth columns give the difference between the computed angles and times of flight and those given in the most trustworthy of the ordinary range tables.

An example is also given (p. 545) of the actual computation of part of a range table for a 12-inch gun and it may be remarked that the whole of the work can be done without reference to any table except that for e^{-x} given in Column III.

NOTES.

Let X, Y, Z be principal axes of a solid of revolution, Z being the generating axis. Let the solid have an angular velocity ω about Z (fig. 5).
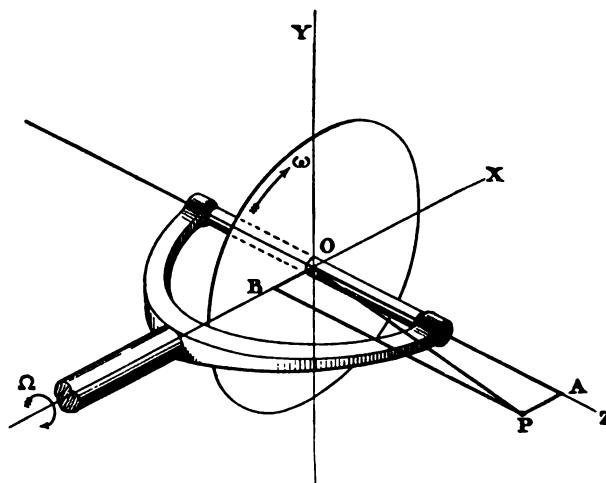
FIG. 5.

Now impose an angular velocity Ω about X, Ω/ω being small (= OB/OA) ; then OP is the instantaneous axis of rotation, and OP (to the first degree of approximation) = OA.

Imagine the solid compressed in the direction of Z until it becomes a circular disc in the plane XY, and let M be its mass and K its radius of gyration about a diameter.

The disc is revolving about OP with velocity ω. The components of the centrifuga

force of the disc parallel to Y exactly balance one another, but as regards the components parallel to X, since half the disc is on one side of the plane through O perpendicular to OP and half on the other, there will be a couple acting on the disc in the plane XZ, tending to make the plane of the disc coincide with the plane perpendicular to the instantaneous axis.

The magnitude of the couple is the integral of (components of centrifugal force parallel to X of all parts of the disc) × (their distance from Y) × (angle AOP), or

$$MK^2\omega^2\Omega/\omega = MK^2\omega\Omega = Q, \text{ say.}$$

This shows that if the gyrostat is made to turn with velocity Ω about X, the mechanical axis exerts a couple Q on its bearings about the axis of Y, *i.e.*, in the plane of XZ. Conversely, if a couple $-Q$ is made to act on the axis in this plane, the gyrostat will revolve with velocity Ω about X.

Suppose the axis of the couple to make the angles λ, μ, ν with X, Y, and Z respectively, the resolved couples about X, Y, and Z are $Q \cos \lambda$, $Q \cos \mu$, and $Q \cos \nu$. The effect of $Q \cos \nu$ will be merely to slightly alter the value of ω, and we need not further consider this component.

$Q \cos \lambda$ and $Q \cos \mu$ will each cause the mechanical axis to resolve with velocities $\Omega \cos \lambda$ and $\Omega \cos \mu$ in the planes XZ and YZ respectively.

Two particular cases may be noted with reference to a projectile :—

(*a*) When the plane of the couple is always in the plane containing the axis of symmetry and the instantaneous axis of the projectile, the axis of symmetry will describe a cone about the axis of the couple with velocity Ω.

(*b*) If the axis of the couple makes an angle $90° - \psi$ with the axis of symmetry of the projectile, these two axes will approach one another with the velocity $\Omega \sin \psi$ (or $\Omega \psi$ if ψ is small).

Case (*a*) corresponds to the action set up by the line of resistance not passing through the centre of gravity of the projectile, and case (*b*) to the action of the couple due to air friction and wake.

The precessional period T (or the time in which the mechanical axis describes a complete cone) is given by the following relations. If ρ is the radius of curvature of the trajectory and v the linear velocity of the projectile, $\rho\Omega^2 = g$. And since $\Omega T = 2\pi$ and $\rho\Omega = v$, we have

$$T = \frac{2\pi v}{g}, \quad (1) \qquad \Omega = \frac{g}{v}, \quad (2) \qquad \rho = \frac{v^2}{g}. \quad (3)$$

If we take ω, the angular velocity due to rifling, as being such that the shot makes one turn in n calibres, $\omega = \frac{2\pi v}{n D}$, hence the couple $Q (= MK^2\omega\Omega)$ becomes $\frac{W}{g} K^2 \frac{2\pi}{n D}$; or, since K^2 for a circular disc $= \frac{1}{4}R^2$, and modern rifling makes $n = 30$, we find $Q = \frac{WD \cdot 2\pi}{16 \times 30}$, or 0.0131 WD.

Thus the couple varies as the fourth power of the linear dimensions of the projectile and is independent of its velocity. This would be true for the whole length of the trajectory if ω remained equal to $2\pi v/n D$; but there is good reason to believe that the actual value of ω, which is only affected by air friction, does not decrease nearly as rapidly as v, whose variation depends on air resistance.

The couple set up by the air friction and wake at the head and tail of the shot is presumably proportional at any instant to ω^2, to the angle (ψ) which the axis of the projectile makes with the direction of motion, and to some at present unknown function of the velocity $F(v)$. So that $\omega^2\psi F(v)$ must be equal to $MK^2\omega\Omega$ if the axis of the projectile is to keep at a nearly constant angular distance from the direction of motion, or

$$\psi = MK^2\Omega/\omega F(v) = MK^2 g/\omega v F(v). \tag{4}$$

Hence as v diminishes, ψ will have to increase, and it is only while moderate increments of ψ, such as will leave ψ itself small, satisfy the conditions in (4) that the motion is approximately steady.

The upward force (f) due to the inclination of the axis of the projectile to the tangent of the trajectory may be taken as proportional to ψ/R, R being the air resistance, and ψ' the projection of ψ on the vertical plane. So that the effective downward acceleration of the shot is $g-f$.

If the shot is fired at an inclination of a to the horizon, it would, in the absence of any force other than air resistance, have travelled in the time t a distance s $(= v't+\frac{v_2}{a}(1-e^{-at}))$, and have attained a height equal to $s \sin a$ above the ground. If the acceleration $g-f$ be resolved parallel and perpendicular to the original direction of motion, the distance traversed in time t will be $s - \sin a \iint(g-f)\,dt$ parallel to the direction defined by the elevation and $\cos a \iint(g-f)\,dt$ normal to that direction.

The result is that at t the projectile will be exactly under the position s, having fallen through a distance $\iint(g-f)\,dt$.

If we put $\iint(g-f) = \frac{1}{2}g't^2$ (g' may be called the apparent value of gravity) and make $s \sin a = \frac{1}{2}g't^2$, then $s \cos a$ (or, if a is small, s) is the range for elevation a.

By the analysis of a large number of range tables, I find that g' is well represented by the formula

$$g' = g - c\,(u_0 - u),$$

where, if the units are feet and seconds, $c = 8\cdot4/u_0$.

The values thus found are accurate enough for range-table purposes, but experiments are much wanted to determine the real relations between f, ψ,* ω, and a.

In the foregoing formulæ no account is taken of the variation of density of the air at different levels. Many projectiles, however, reach heights at which the variation of density cannot be neglected. A comparatively simple method of correcting the range for varying density is as follows :—The height (h) which projectiles reach with " direct fire " is small compared to H, the height of the homogeneous atmosphere. Thus the (a) of the foregoing formulæ becomes, for a shot at altitude h, $a\,(1 - h/H)$.
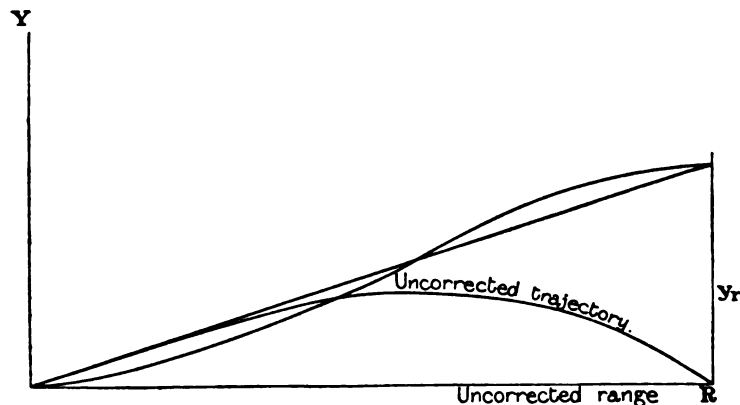
Fig. 6.

* ψ will vary with the shape of the projectile.

In the expression for v, namely $v = v' + u_0 e^{-at}$, suppose t constant and differentiated with respect to a,

$$du/da = -tu_0 e^{-at} = -tv.$$

Thus

$$v + \delta v = v' + u(1 - t\delta a), \quad \text{but} \quad \delta a = -ah/\mathrm{H};$$

therefore

$$v + \frac{dv}{dn}\,\delta h = v' + v\left(1 + at\,\frac{h}{\mathrm{H}}\right).$$

Now, with the range ($s\cos a$) as abscissa, draw a curve with ordinate y such that

$$\frac{d\mathrm{R}}{(d\mathrm{R}^2 + dy^2)^{\frac{1}{2}}} = \frac{v' + u}{v' + u(1 + ath/\mathrm{H})} \, .$$

Then the length of this curve is the range corrected for variation of density.*

The form of the curve is shown in the diagram, fig. 6, and an approximation to its length is $(\mathrm{R}^2 + y_r^2)^{\frac{1}{2}}$.

It will be found that for the larger guns the angle $\sin^{-1}(y_\mathrm{R})/\mathrm{R}$ is of the same order of magnitude as a, that the corrected range is nearly equal to s; and it is for this reason that the formula range $= s$ (instead of $s\cos a$) is practically correct, even when the angle of elevation is as large as $9°$. For small arms the range given by the formula would be slightly in excess of the true range with elevation as large as this.

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* The height which the projectile reaches in time t varies with the density of the air, but for the purpose of correcting the range it is sufficient to take h as what it would have been with air of constant density.

On the Force required to Stop a Moving Electrified Sphere.

' By G. F. C. Searle, M.A., F.R.S., University Lecturer in Experimental
Physics, Cambridge.

§ 1. *Energy of a Charged Sphere in Steady Motion: Heaviside's Method.*—
When the velocity of a system of electric charges is changed in any manner,
waves of disturbance travel out from the system in all directions with velocity
v, the speed of light, and carry both energy and momentum* to the distant
parts of the electro-magnetic field. Dr. Oliver Heaviside† was the first to
notice that these waves might be made to yield important information as to
energy and momentum of the moving system. Thus, when a charged sphere
is in steady motion the electro-magnetic field possesses electric energy U,
magnetic energy T and momentum M. If, now, the sphere be suddenly
brought to rest, the forces which hold it at rest do no work, since their points
of application do not move, and hence the total energy in the field is the
same after the sphere is brought to rest as it was before. When the sphere is
stopped, a pulse with depth equal to the diameter of the sphere travels
outwards. The electric and magnetic forces in this pulse ultimately vary
inversely as the distance and hence the energy and the momentum in the
pulse tend to constant values as the pulse travels out to infinity. Outside the
pulse the electric and magnetic forces are the same as if the sphere had
continued in steady motion and therefore are, after an infinite time, inversely
proportional to the square of the distance from the point which the centre of
the sphere would have reached had its motion continued. Hence the energy
and momentum outside the pulse ultimately vanish. On the other hand, the
field within the spherical region bounded by the pulse is the same as that
due to the sphere at rest and hence the energy in this part of the field is
ultimately U$_s$, the electrostatic energy of the sphere at rest. Thus, if W be
the limiting value of the energy in the pulse, the energy in the field is
ultimately U$_s$+W. But, before the sphere was stopped, the energy was
U+T. Hence,

$$U+T = U_s+W. \qquad (1)$$

Dr. Heaviside calculated W for the pulse due to a sphere with a surface-
charge and so found U+T, his value for U+T agreeing with that which I

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* The momentum per unit volume is $(\mu K/4\pi)\,\mathbf{VEH}$, where $\mathbf{VEH}$ is the vector product
of the electric and magnetic forces.

† 'The Electrician,' November 29, 1901, p. 210. See also Searle, 'Phil. Mag.,' January,
1907, p. 131.

had previously found by a direct integration of the energy in the field of a moving sphere, the integration extending through all space.[*]

Dr. Paul Hertz[†] has applied this method to a sphere with a uniform volume-charge and has shown that the energy and momentum of the sphere in steady motion are six-fifths of the energy and momentum of a sphere of the same radius with an equal surface-charge. He has also indicated how the method may be applied to any system whatever, and I have shown how to carry out the details of calculation in the cases of a charged ellipsoid of revolution moving along its axis and of a charged disc moving in its own plane.[‡]

§ 2. *Force required to Start a Charged Sphere: Paul Hertz's Method.*—But this list does not by any means exhaust the possibilities of the method of pulses.[§] For Dr. Hertz has applied it to determine the force which must be applied to a sphere with either a volume- or a surface-charge to cause the sphere to start suddenly from rest and then to move uniformly along a straight line with any velocity u not greater than v, the velocity of light.

If F be the required force, the work done by F when the sphere has been in motion for a time t is

$$\int_0^t \mathrm{F}u\,dt.$$

Before the sphere began to move the energy in the field was U_s. After the time t it is

$$U_s + \int_0^t \mathrm{F}u\,dt.$$

If at the time t the sphere be suddenly brought to rest, the stopping forces do no work and hence the energy in the field remains unchanged. After an infinite time the energy in the field consists of U_s together with W', the energy in the compound pulse formed by the pair of pulses generated by starting and stopping the sphere.

Hence
$$U_s + W' = U_s + \int_0^t \mathrm{F}u\,dt,$$

or
$$\mathrm{F} = \frac{1}{u}\frac{dW'}{dt}. \tag{2}$$

It must be noticed that the two pulses are not concentric, since their centres are separated by the distance ut. In the case of a sphere with a surface-charge, the pulses destroy each other's effects where they overlap, since the electric and magnetic forces caused by the sudden stopping of the sphere are

[*] 'Phil. Mag.,' Oct., 1897.

[†] "Untersuchungen über unstetige Bewegungen eines Electrons," 'Inaugural Dissertation,' Göttingen, 1904, p. 49. See also Searle, 'Phil. Mag.,' January, 1907, p. 132.

[‡] 'Phil. Mag.,' January, 1907.

[§] 'Dissertation,' p. 65.

equal in magnitude and opposite in direction to those caused by the starting of the sphere, and are also constant throughout the depth of each pulse. For a sphere with a volume-charge, E and H are not constant throughout the depth of each pulse and the calculation then becomes a little more complicated.

It is necessary to distinguish three stages in the process of starting the sphere. If a be the radius of the sphere, the first stage lasts from $t = 0$ to $t = 2a/(v+u)$, the second from $t = 2a/(v+u)$ to $t = 2a/(v-u)$ and the third from $t = 2a/(v-u)$ onwards. If F_1, F_2 and F_3 denote the forces required in the three stages and if k stand for $1-u/v$, Dr. Hertz's results are as follows:—

Sphere with Uniform Surface-charge Q.

$$F_1 = \frac{Q^2}{2Ka^2}\left\{\frac{v}{u}-\frac{v^2-u^2}{2u^2}\log\frac{v+u}{v-u}\right\}, \tag{3}$$

$$F_2 = \frac{Q^2}{2Ka^2}\left\{\frac{1}{4}+\frac{v}{2u}-\frac{3v^2}{4u^2}+\frac{2av}{u^2t}-\frac{a^2}{u^2t^2}+\frac{v^2-u^2}{2u^2}\log\frac{(v-u)t}{2a}\right\},$$

$$F_3 = 0.$$

Thus, in the first stage the force is constant, while in the third stage it is zero.

When u tends to equality with v, the expressions tend to the following limits:—

$$F_1 = \frac{Q^2}{2Ka^2}, \qquad\qquad t < a/v,$$

$$F_2 = \frac{Q^2}{2Ka^2}\left\{\frac{2a}{vt}-\frac{a^2}{v^2t^2}\right\} \qquad t > a/v.$$

There is no third stage now, since the second stage extends from $t = a/v$ to infinite values of the time.

Sphere with Uniform Volume-charge Q.

$$F_1 = \frac{Q^2u}{8Ka^6v}\left\{16a^3vt-12a^2v^2t^2+\left(1+\frac{3u^2}{5v^2}\right)v^4t^4\right\}, \tag{4}$$

$$F_2 = \frac{Q^2u^2}{8Ka^6v^2}\left\{-\frac{4a^6}{v^2t^2}+\frac{48a^5}{5vt}+(-18k+9k^2)a^4\right.$$
$$+(12k^2-8k^3)a^3vt+\left(-3k^3+\frac{9k^4}{4}\right)a^2v^2t^2$$
$$\left.+\left(\frac{3k^5}{40}-\frac{k^6}{16}\right)v^4t^4\right\},$$

$$F_3 = 0.$$

When $u = v$, so that $k = 0$, the expressions become

$$F_1 = \frac{Q^2}{8Ka^6}\,(16a^3vt - 12a^2v^2t^2 + \tfrac{8}{5}v^4t^4), \qquad t < a/v, \qquad (4a)$$

$$F_2 = \frac{Q^2}{8Ka^6}\left(-\frac{4a^6}{v^2t^2} + \frac{48a^5}{5vt}\right). \qquad\qquad t > a/v.$$

§ 3. *Force required to stop a Moving System. Pulse Method.*—I find that, if Dr. Hertz's work be slightly extended, the force required to suddenly stop a charged system is easily calculated. For the sake of simplicity, the investgation will be limited to the case in which the momentum of the system in steady motion, as well as the momentum in the pulse formed when it is stopped, are parallel to the direction of motion. If F be the force which must be applied to the system at any time t, after it has been brought to rest at $t = 0$, the positive direction of F being opposite to that of u, then F is also the force which the electro-magnetic field exerts on the system in the direction of u.

The momentum given up by the electro-magnetic field from $t = 0$ to $t = t$ is

$$\int_0^t F\,dt.$$

During this period the force F does no work, since the system is at rest, and hence the energy of the system is unchanged during this period.

At the time t let the system be restarted with the same velocity u without change of direction, and let G be the force which must be applied to the system at any subsequent time in the direction of u in order to maintain the velocity u. This force lasts from $t = t$ to $t = t'$, where $t' - t$ is determined by the condition that in the time $t' - t$ the pulse formed on restarting the system has completely passed over the system. When $u = v$, the time $t' - t$ is infinite. During the interval $t' - t$, the momentum of the system is increased by

$$\int_t^{t'} G\,dt,$$

and hence the total gain of momentum is

$$\int_t^{t'} G\,dt - \int_0^t F\,dt.$$

During the interval $t' - t$, the energy of the system has been increased by

$$u\int_t^{t'} G\,dt.$$

The stopping and the restarting of the system each give rise to a pulse, and the compound pulse so formed carries off energy W′ and momentum P′.

Before the system was stopped the energy of the electro-magnetic field was $U + T$ and its momentum was M, and at an infinite time after the stopping and restarting the energy is $U + T + W'$ and the momentum is $M + P'$, since the energy and momentum in the parts of the field outside the compound pulse ultimately vanish.

Equating the two expressions for the gain of momentum, we have

$$\int_t^{t''} G\,dt - \int_0 F\,dt = P'.$$

Similarly,

$$u \int_t^{t'} G\,dt = W'.$$

Hence

$$\int_0^t F\,dt = W'/u - P', \qquad (5)$$

and thus we find that the force required to stop the system is given by

$$F = \frac{d}{dt}\left(\frac{W'}{u} - P'\right). \qquad (6)$$

This force will become zero as soon as $W'/u - P'$ becomes constant, which will occur as soon as t is so great that the two pulses due to the stopping and restarting do not overlap.

Since the system is restarted from the position in which it was stopped, the two pulses are concentric, though their radii differ by vt, for one pulse is formed at $t = 0$ and the other at the time t. The fact that the pulses are concentric introduces an element of simplicity into the calculations.

The whole momentum I, given up by the electro-magnetic field during the time for which the stopping force lasts, is found by taking t so great that the two pulses do not overlap. In this case each pulse has the same energy and the same momentum, and hence, if W and P be the energy and the momentum in each of the separate pulses, $W' = 2W$ and $P' = 2P$.

Hence

$$I = \int_0^t F\,dt = 2\left(\frac{W}{u} - P\right). \qquad (7)$$

§ 4. *Force required to stop a Sphere with Surface-charge.*—We may now apply the results of § 3 to find the force required to stop a sphere of radius a with a uniform surface-charge Q. If W_0 be the energy and P_0 the momentum sent out in the pulse formed when the velocity u is suddenly destroyed, we have*

$$W_0 = \frac{Q^2}{2Ka}\left\{\frac{v}{u}\log\frac{v+u}{v-u} - 2\right\}. \qquad (8)$$

$$P_0 = \frac{Q^2}{2Kau}\left\{\left(\frac{3v}{2u} - \frac{u}{2v}\right)\log\frac{v+u}{v-u} - 3\right\}. \qquad (9)$$

* See Searle, 'Phil. Mag.,' Jan., 1907, pp. 131, 132.

Hence $$\frac{W_0}{u} - P_0 = \frac{Q^2}{2Kav} \left\{ \frac{v}{u} - \frac{v^2 - u^2}{2u^2} \log \frac{v+u}{v-u} \right\}. \tag{10}$$

If the time t be less than $2a/v$, the two pulses will overlap over a depth $2a - vt$, and in this part the electric and magnetic forces due to one pulse will exactly neutralise those due to the other, since these forces are constant throughout the depth of either pulse. There remain two shells, each of depth vt, where the forces do not cancel. The total energy W' and the total momentum P' in the compound pulse are therefore given by

$$W' = 2vt \frac{W_0}{2a}, \qquad P' = 2vt \frac{P_0}{2a}.$$

Hence, if F_0 be the force required to stop the sphere with a surface-charge, we have, by (6),

$$F_0 = \frac{v}{a} \left(\frac{W_0}{u} - P_0 \right)$$

$$= \frac{Q^2}{2Ka^2} \left\{ \frac{v}{u} - \frac{v^2 - u^2}{2u^2} \log \frac{v+u}{v-u} \right\}. \tag{11}$$

Hence the force is constant during the time $2a/v$ for which it acts. The impulse, I_0, of this force, or the momentum which the electro-magnetic field gives up to the agent stopping the sphere, is $2aF_0/v$.

Hence $$I_0 = \frac{Q^2}{Kav} \left\{ \frac{v}{u} - \frac{v^2 - u^2}{2u^2} \log \frac{v+u}{v-u} \right\}. \tag{12}$$

When u tends to equality with v, so that the initial velocity of the sphere becomes more and more nearly equal to the velocity of light, the expression for the force tends to a limit. For as $v - u$ tends to zero, $(v-u) \log (v-u)$ tends to the limit zero, and hence F_0 tends to the limit

$$F_0 = \frac{Q^2}{2Ka^2}. \tag{13}$$

The formula (11) gives us no information as to the value of F_0 when u is equal to v, since the expression then becomes indeterminate. But, instead of deducing the force F_0 from the energy and momentum in the compound pulse, we can (as in § 6) calculate its value, when $u = v$, by direct integration of E_x over the surface of the sphere, where E_x is the component, parallel to the direction of u, of the electric force in the pulse. We then find that the value of F_0 for $u = v$ is identical with the limit $Q^2/2Ka^2$ of the general value of the force. Hence, there is no discontinuity in the force when $u = v$.

When u/v is very small, we have, by (11),

$$F_0 = \frac{Q^2 u}{3Ka^2 v}. \tag{14}$$

§ 5. *Force required to Stop a Sphere with Volume-charge.*—When the sphere of radius a has a uniform volume-charge Q, the calculation of the force required to stop the sphere is a little more difficult, because the electric and magnetic forces are not constant throughout the depth of the pulse formed on suddenly starting or stopping the sphere.   If we take two parallel planes at distances z and $z+dz$ from the surface of the sphere, and if dQ be the charge between them,

$$\frac{d\mathrm{Q}}{dz} = \frac{3\mathrm{Q}z\,(2a-z)}{4a^3}.$$

As H. A. Lorentz[*] and Paul Hertz[†] have pointed out, at a great time after the formation of one of these pulses the electric and magnetic forces at a point on the radius normal to these planes, and at a distance z from the outer surface of the pulse, are proportional to $d\mathrm{Q}/dz$.

There are two parts of the compound pulse where the separate pulses due to the stopping and the restarting of the sphere do not overlap, and in each of these parts, of depth vt, there are equal amounts of energy and of momentum.   Now, when a pulse is generated by starting or stopping an equal sphere with a surface-charge Q, the energy per unit depth of pulse is $\mathrm{W}_0/2a$, where W_0 is given by (8), while for this case $d\mathrm{Q}/dz = \mathrm{Q}/2a$. Hence, if W_1 be the energy in the part of the compound pulse where the separate pulses do not overlap,

$$\mathrm{W}_1 = 2\,\frac{\mathrm{W}_0}{2a}\int_0^{vt}\!\left(\frac{d\mathrm{Q}}{dz}\right)^2\!\left(\frac{2a}{\mathrm{Q}}\right)^2 dz$$

$$= \frac{\mathrm{W}_0}{a}\int_0^{vt}\!\left\{\frac{3z\,(2a-z)}{2a^2}\right\}^2 dz$$

$$= \frac{3\mathrm{W}_0 v^2 t^2}{8a^5}\left\{8a^2 vt - 6av^2 t^2 + \tfrac{8}{5}v^3 t^3\right\}.$$

In that part of the compound pulse where the two separate pulses overlap, the effective value of $d\mathrm{Q}/dz$ is

$$\frac{3\mathrm{Q}z\,(2a-z)}{4a^3} - \frac{3\mathrm{Q}\,(z-vt)(2a-z+vt)}{4a^3},$$

or

$$\frac{3\mathrm{Q}vt}{4a^3}\,(2a + vt - 2z),$$

since the electric and magnetic forces have opposite directions in the two separate pulses, and since the outer surfaces of the two pulses are separated by the distance vt.   This part of the compound pulse extends from $z = vt$ to $z = 2a$, and hence, if W_2 be the energy in this part, we have

* ' Encyklopädie der Mathematischen Wissenschaften,' "Electronentheorie," p. 188.
† 'Dissertation,' p. 36.   See also Searle, ' Phil. Mag.,' January, 1907, p. 123.

$$W_2 = \frac{W_0}{2a} \int_{vt}^{2a} \left(\frac{dQ}{dz}\right)^2 \left(\frac{2a}{Q}\right)^2 dz$$

$$= \frac{W_0}{2a} \int_{vt}^{2a} \left\{ \frac{3vt \,(2a + vt - 2z)}{2a^2} \right\}^2 dz$$

$$= \frac{3W_0 v^2 t^2}{8a^5} (2a - vt)^3.$$

Hence, if W' be the energy in the compound pulse,

$$W' = W_1 + W_2 = \frac{3W_0 v^2 t^2}{8a^5} (8a^3 - 4a^2 vt + \tfrac{4}{5} v^3 t^3). \tag{15}$$

Similarly, if P_0 be the momentum in the pulse formed on starting a sphere with a surface-charge, where P_0 is given by (9), the momentum in the compound pulse is given by

$$P' = \frac{3P_0 v^2 t^2}{8a^5} (8a^3 - 4a^2 vt + \tfrac{4}{5} v^3 t^3). \tag{16}$$

We can now find the force required to stop the sphere, for we have, by (6),

$$F = \frac{d}{dt}\left(\frac{W'}{u} - P'\right)$$

$$= \frac{3v}{8a^5} (16a^3 vt - 12a^2 v^2 t^2 + v^4 t^4)\left(\frac{W_0}{u} - P_0\right)$$

$$= \frac{3v}{8a^5} vt \,(2a - vt)^2 (4a + vt)\left(\frac{W_0}{u} - P_0\right)$$

$$= \frac{3Q^2}{16Ka^6} (16a^3 vt - 12a^2 v^2 t^2 + v^4 t^4)\left(\frac{v}{u} - \frac{v^2 - u^2}{2u^2}\log\frac{v+u}{v-u}\right). \tag{17}$$

If I be the total momentum given up by the electro-magnetic field when the sphere is stopped, we have, by (7),

$$I = 2\,(W/u - P).$$

But, as Dr. Hertz[*] has shown, $W = \tfrac{4}{5} W_0$ and $P = \tfrac{4}{5} P_0$, and, hence, $I = \tfrac{4}{5} I_0$, where I_0 is given by (12).

The same result follows if we integrate the expression (17) with respect to the time from $t = 0$ to $t = 2a/v$, for

$$\int_0^{2a/v} F\,dt = \tfrac{4}{5} \cdot 2\left(\frac{W_0}{u} - P_0\right) = \tfrac{4}{5} I_0.$$

When u tends to equality with v, we see, by (17), that F tends to the limit

$$F = \frac{3Q^2}{16Ka^6} (16a^3 vt - 12a^2 v^2 t^2 + v^4 t^4). \tag{18}$$

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[*] 'Dissertation,' p. 49. See also Searle, 'Phil. Mag.,' January, 1907, p. 132.

It is proved by another method in § 7 that the value of F for $u = v$ is equal to the limit (18).

When u^2/v^2 is very small, we have, by (10),

$$\frac{W_0}{u} - P_0 = \frac{Q^2 u}{3Kav^2},$$

and then (17) becomes

$$F = \frac{Q^2 u}{8Ka^6 v}(16a^3 vt - 12a^2 v^2 t^2 + v^4 t^4). \tag{19}$$

If F_0 be the force required to stop the sphere with a surface-charge, so that F_0 is given by (11), we can write (17) in the form

$$F = \tfrac{3}{8}a^{-4}(16a^3 vt - 12a^2 v^2 t^2 + v^4 t^4)\, F_0. \tag{20}$$

The maximum value of F occurs when $vt = a(\sqrt{3}-1)$ and the maximum value is

$$F_{\text{max}} = 9(\sqrt{3}-\tfrac{3}{2})\, F_0 = 0.209\, F_0.$$

§ 6. *Force required to Stop a Sphere with Surface-charge when* $u = v$.—We now pass on to calculate by a direct method the force required to stop a sphere with a surface-charge, when the initial velocity of the sphere is equal to that of light. We now find the force experienced by each element of the charge at a time t after the sphere has been brought to rest, and then integrate over the surface of the sphere.

When an elementary charge dQ is suddenly stopped, the electric force in the pulse is given by[*]

$$dE = \frac{u \sin \gamma}{Kr\,(v - u \cos \gamma)}\, \frac{dQ}{p}. \tag{21}$$

Here $r = vt$ is the distance from the point where the charge is stopped and γ is the angle between the radius r, drawn *from* that point, and the direction of the initial velocity u. Further, p is the infinitesimal width of the charge measured in a direction parallel to r. The electric force dE is in the plane of r and u, and is at right angles to r, while it has a *positive* component in the direction of u.

If dE_x be the component of dE in the direction of u, we find that, when $u = v$,

$$dE_x = dE \sin \gamma = \frac{dQ\,(1 + \cos \gamma)}{Krp}. \tag{22}$$

Let O (fig. 1) be the centre of the sphere after it has been brought to rest and let OA be the direction of its initial velocity. Let P be a point on the surface of the sphere and let POA $= \theta$. About P as centre describe two

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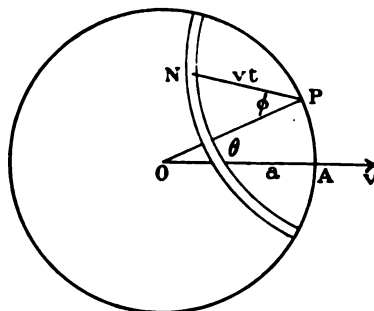
Fig. 1.

spheres of radii r and $r+dr$, cutting the charged sphere in two circles. Let N be a point on the band bounded by these circles, let NPO $= \phi$, and let the plane NPO be inclined at an angle ψ to the plane POA.

Since $r = 2a \cos \phi$, we have $dr = -2a \sin \phi d\phi$. But the angle subtended at O by the width of the band is twice the angle subtended at P, and is, therefore, $-2d\phi$, and thus the width of the band is $-2ad\phi$ or $dr/\sin \phi$. If the charge on that element of the ring which is defined by the planes ψ and $\psi + d\psi$ be dQ, then

$$dQ = \frac{Q}{4\pi a^2}(-2ad\phi)\, r \sin \phi d\psi,$$

while

$$p = dr = -2a \sin \phi d\phi.$$

Hence

$$\frac{dQ}{p} = \frac{Qrd\psi}{4\pi a^2},$$

and thus, by (22),

$$d\mathbf{E}_x = \frac{Q\,(1+\cos \gamma)\,d\psi}{4\pi K a^2}. \tag{23}$$

It is only the band defined by r, where $r = vt$, which acts upon P by its pulse at the time t, and hence we obtain the complete value of the part of $\mathbf{E}_x$ which is due to the action of pulses by integrating (23) with respect to ψ.

Now $r \cos \gamma$ is the projection of NP (*not* PN) upon OA, and thus we easily find—

$$\cos \gamma = \cos \theta \cos \phi + \sin \theta \sin \phi \cos \psi. \tag{24}$$

Hence

$$\mathbf{E}_x = \int_0^{2\pi} \frac{d\mathbf{E}_x}{d\psi}\, d\psi = \frac{Q\,(1+\cos \theta \cos \phi)}{2K a^2};$$

but $\cos \phi = r/2a = vt/2a$, and thus

$$\mathbf{E}_x = \frac{Q}{2K a^2}\left(1 + \frac{vt \cos \theta}{2a}\right). \tag{25}$$

The element of charge at P is also acted on by the charges on the sphere whose distances from P are less than vt, as well as by those whose distances

are greater than vt. The elements within the distance vt act on the element at P according to the ordinary electrostatic law, and the element at P acts on them in the same way. Hence the actions between the element at P and the elements within the distance vt are in equilibrium, and may be left out of account in estimating the force exerted on the sphere as a whole. The elements outside the distance vt act on the element at P in the same way as if they had continued to move on with the speed of light. The electric forces due to these elements are therefore at right angles to the direction of u, and therefore contribute nothing to the total force.

Hence, if F_0 be the total force experienced by the sphere at time t, we can find F_0 by intergrating (25) over the surface of the sphere. Thus—

$$F_0 = \int_0^\pi \frac{E_x Q}{4\pi a^2} 2\pi a^2 \sin\theta\, d\theta = \frac{Q^2}{4Ka^2} \int_0^\pi \left(1 + \frac{vt \cos\theta}{2a}\right) \sin\theta\, d\theta = \frac{Q^2}{2Ka^2}. \quad (26)$$

This value is equal to the limit (13) to which (11), the general expression for the force, tends as u tends to equality with v. The force experienced by the sphere has this value for the time $2a/v$ during which the pulse is passing over the sphere. As soon as the pulse is clear of the sphere the force vanishes.

§ 7. *Force required to Stop a Sphere with Volume-charge when $u = v$.*—The method of § 6 may be applied to find the force required to suddenly stop a sphere with a uniform volume-charge, when the initial velocity is equal to that of light.

In fig. 2, O is the centre of the sphere after it has been brought to rest, OA is the direction of its original velocity, and P is any point within the
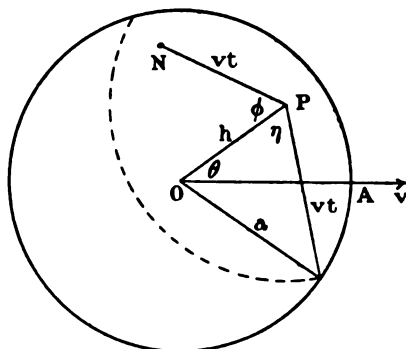
Fig. 2.

sphere. Let $OP = h$ and $POA = \theta$, and let OA be taken as the axis of x. Let N be a point in the sphere at a distance $r = vt$ from P, let $NPO = \phi$, and let the plane NPO be inclined at an angle ψ to the plane POA.

The charge per unit volume is $3Q/4\pi a^3$, and thus the x-component of the electric force at P due to the pulse arising from stopping the charge (of thickness $p = dr$) included in the elementary volume $r^2 \sin \phi\, d\phi\, d\psi\, dr$ is, by (22),

$$d\mathbf{E}_x = \frac{3Qr^2 \sin \phi\, d\phi\, d\psi\, dr}{4\pi a^3 . dr} \cdot \frac{1+\cos \gamma}{Kr},$$

where $\cos \gamma$ is given by (24).

Since $r = vt$, we have

$$d\mathbf{E}_x = \frac{3Qvt}{4\pi a^3 K} \sin \phi\, (1+\cos \gamma)\, d\phi\, d\psi.$$

The x-component of the electric force at .P at time t due to pulses is obtained by integrating this expression over that part of the surface of the sphere of centre P, and of radius vt, which lies within the charged sphere. For the reasons explained in § 6 the force experienced by the *whole* sphere is equal to that due to the action of the pulses alone.

When the sphere of radius vt lies entirely within the charged sphere, ψ goes from 0 to 2π and ϕ from 0 to π. In this case we have

$$\mathbf{E}_x = \frac{3Qvt}{4\pi a^3 K} \int_0^\pi \int_0^{2\pi} \sin \phi\, (1+\cos \gamma)\, d\phi\, d\psi$$

$$= \frac{3Qvt}{2a^3 K} \int_0^\pi \sin \phi\, (1+\cos \theta \cos \phi)\, d\phi$$

$$= \frac{3Qvt}{a^3 K} . \tag{27}$$

When the sphere of radius vt lies partly outside the charged sphere, ψ goes from 0 to 2π, while ϕ goes from 0 to η, where η is the angle subtended at P by a radius drawn from O to a point on the circle of intersection of the two spheres. From the triangle having this radius as base and P as vertex we have

$$\cos \eta = \frac{h^2 + v^2 t^2 - a^2}{2hvt} . \tag{28}$$

In this case we have

$$\mathbf{E}_x = \frac{3Qvt}{2a^3 K} \int_0^\eta \sin \phi\, (1+\cos \theta \cos \phi)\, d\phi$$

$$= \frac{3Qvt}{2a^3 K} \{1 - \cos \eta + \tfrac{1}{2} \cos \theta\, (1-\cos^2 \eta)\}. \tag{29}$$

The time of passage of the whole pulse across the sphere may be divided into two stages. In the first stage, which lasts from $t = 0$ to $t = a/v$, some complete spheres of radius vt can be described, but in the second stage, lasting from $t = a/v$ to $t = 2a/v$, the spheres of radius vt are all incomplete.

In the first stage we can describe complete spheres of radius vt about every point within the sphere of centre O and radius $a - vt$.

Now, by (27), E_x has the constant value $3Qvt/a^3K$ throughout the sphere of radius $a - vt$. The charge within that sphere is $Q(a - vt)^3/a^3$, and hence, if X_1 be the force on this part of the charged sphere,

$$X_1 = \frac{3Qvt}{a^3K} \cdot \frac{Q(a-vt)^3}{a^3} = \frac{3Q^2vt(a-vt)^3}{Ka^6}.$$

If X_2 be the force on the spherical shell of radii $a - vt$ and a, then X_2 is due to the action of incomplete spheres, and thus—

$$X_2 = \frac{3Q}{4\pi a^3} \cdot \int_0^\pi \int_{a-vt}^a E_x \cdot 2\pi h^2 \sin\theta \, d\theta dh,$$

where E_x is now given by (29). When we integrate with respect to θ, the term in E_x involving $1 - \cos^2\eta$ vanishes, and thus, substituting for $\cos\eta$ from (28), we find

$$X_2 = \frac{9Q^2vt}{2Ka^6} \int_{a-vt}^a \left(1 - \frac{h^2 + v^2t^2 - a^2}{2hvt}\right) h^2 dh$$

$$= \frac{3Q^2v^2t^2}{Ka^6} \left(\tfrac{9}{4}a^2 - 3avt + \tfrac{5}{16}v^2t^2\right).$$

The resultant force F is equal to $X_1 + X_2$, and thus

$$F = \frac{3Q^2vt}{Ka^6} \left\{(a-vt)^3 + \tfrac{9}{4}a^2vt - 3av^2t^2 + \tfrac{5}{16}v^3t^3\right\}$$

$$= \frac{3Q^2}{16Ka^6} \left\{16a^3vt - 12a^2v^2t^2 + v^4t^4\right\}. \tag{30}$$

In the second stage from a/v to $2a/v$, no complete sphere of radius vt can be described about any point within the charged sphere. But in this case we need not integrate throughout the whole volume of the sphere, since the pulses due to all the elements of the sphere have now completely passed over the part enclosed by the sphere $h = vt - a$, and have left this part free from any force due to pulses.

Integrating throughout the spherical shell of radii $vt - a$ and a, we find, for the force during the second stage,

$$F = \frac{3Q}{4\pi a^3} \int_0^\pi \int_{vt-a}^a E_x \cdot 2\pi h^2 \sin\theta d\theta dh,$$

where E_x is given by (29). Thus

$$F = \frac{9Q^2vt}{2Ka^6} \int_{vt-a}^a \left(1 - \frac{h^2 + v^2t^2 - a^2}{2hvt}\right) h^2 dh$$

$$= \frac{3Q^2}{16Ka^6} \left\{16a^3vt - 12a^2v^2t^2 + v^4t^4\right\}. \tag{31}$$

This expression is identical with that given by (30) for the force during the first stage. Hence, the force is expressed by the same formula during the whole time of its action. The value also agrees with the limit (18) approached by (17), the general value of the force, as found in § 5, when u tends to equality with v.

§ 8. *Comparison of Forces required for Starting and Stopping a Charged Sphere.*—It is interesting to compare Dr. Hertz's value for the force required during the first stage of starting the sphere with the value obtained in the present paper for the force required to stop the sphere.

Sphere with a Surface-charge.

From (3) and (11) it will be seen that the stopping force is identical with the starting force during the first stage of the motion. This result could have been foretold without any detailed calculation. For it is easily seen that Dr. Hertz's method leads to a starting force which is constant during the first stage, while my method leads to a constant stopping force. When $t = 0$, the two forces must be equal, since the sphere is at that time in the same position relative to the pulses as it is when it is suddenly stopped. Thus, since each force is constant, they remain equal up to the time $2a/(v+u)$.

Sphere with a Volume-charge.

The method employed in the case of a surface-charge shows that the forces must be equal at $t = 0$. But since dQ/dz is zero at the surface of the sphere, it is easily seen that both the starting and the stopping forces must vanish at $t = 0$. This result also follows from the detailed formulæ (4) and (17), since each expression contains t as a factor.

But when u/v is infinitesimal, the displacement of the sphere during the time $2a/(v+u)$, when it is started, is also infinitesimal, and hence for such a value of u/v the force required during the first stage of the starting of the sphere must be equal to that required to stop it. The latter force lasts for $2a/v$, but, since u/v is infinitesimal, the first stage may be considered to last for the same time. Comparing Dr. Hertz's expression (4) with (19), it will be seen that they agree when u^2/v^2 is negligible in comparison with unity.

The length of the second stage is from $2a/(v+u)$ to $2a/(v-u)$, and thus may be considered as zero.

When $u = v$, it appears from (4a) and (31) that, as long as v^2t^2 is negligible compared with a^2, the stopping force is three halves of the starting force.

Studies of the Processes operative in Solutions.—Parts II–V.

By H. E. Armstrong, F.R.S., and others.

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II. *The Displacement of Chlorides from Solution by Alcohol and by Hydrogen Chloride.* By H. E. Armstrong, F.R.S., J. V. Eyre, Ph.D., A. V. Hussey and W. P. Paddison.

Although innumerable determinations of solubility have been placed on record, little has been done to elucidate the phenomena of what may be termed competitive dissolution. A comprehensive series of determinations of the solubility of chlorides in presence of hydrogen chloride made by Engel[*] led him to the conclusion that, up to a certain point, the hydride displaces the salt approximately equivalent by equivalent, the sum of the equivalents being practically constant ; eventually, however, in every case, the chloride falls off in displacing power. Almost the only attempt to deal with the problem in a rational manner is that made by Nernst in 1888, who discussed the mutual influence which salts exercise on one another on the assumption that the gas laws are applicable to liquids and from the ionic dissociation standpoint. Having in mind the fact that, although neutral gases are without influence, a separation of ammonium chloride at once takes place if either hydrogen chloride or ammonia be introduced into a space in which these products of its dissociation are in equilibrium with the chloride, Nernst[†] advocated the view that the degree of dissociation of a dissolved salt—and therefore its solubility—will be diminished if a compound containing either of the ions of the salt be introduced into the solution. In support of this contention, results were put forward showing that the solubility of silver acetate is diminished and to about an equal extent by equivalent amounts of

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[*] 'Ann. Chim. Phys.,' 1888, [6], vol. 13, p. 370.
[†] 'Zeits. Phys. Chem.,' 1889, vol. 4, p. 372.

the electrolytes sodium acetate and silver nitrate—which are supposed to undergo dissociation in solution to about equal extents; whilst acetic acid—which is supposed to exist in aqueous solution almost undissociated—has little if any influence. The subject was subsequently dealt with more fully from the same point of view by A. A. Noyes.*

The circumstance that " unionisable " (by hypothesis undissociated) neutral substances such as methylic and ethylic alcohol are powerful precipitants was ignored by Nernst and Noyes.

Unfortunately, the data which have been placed upon record (irrespective of difficulties arising from the irregularity of the curves which they afford) are seldom sufficient for the satisfactory discussion of the problem of competitive solubility. In but few cases has the influence of one substance on another been determined in a graduated manner, saturated solutions alone having been dealt with by most observers.

In making the experiments to be referred to in this communication, alcohol and hydrogen chloride were chosen as precipitants of a number of chlorides because the one may be regarded as a representative non-electrolyte and a weak dehydrant, the other as a representative electrolyte and moderately powerful dehydrant. The main object in view being to determine their relative " concentrating effects " in competition with that of the salts selected, *weight-normal* solutions were used throughout the inquiry—*i.e.*, solutions containing in 1000 grammes of water a known proportion of the substance whose effect was to be determined in competition with that of another.† By operating in this way, the effect was ascertained which the

* *Ibid.,* 1890, vol. 6, p. 491.

† The saturated solutions were prepared by vigorously stirring the solid salt with the solvent in a large test tube (21 cm. by 3 cm.) supported in a large water bath, either a rectangular tank provided with a glass front and back or a deep circular pan; the temperature was carefully maintained at 25° by means of a spiral toluene gas regulator, whilst both bath and solvent were constantly stirred by means of a motor. The saturated solution was withdrawn by means of a pipette provided with a graduated neck and stop-cock (comp. Lowry, 'Chem. Soc. Trans.,' vol. 89, p. 1036).

The density of the alcohol used was $d \frac{19°}{19}$ 0·79405 ; the alcoholic solutions were prepared by weighing.

In the actual experiments, while the solid was being stirred with the solvent, the dried, weighed pipette was kept in a cylinder standing in the bath. Usually stirring was interrupted at the end of an hour; then as soon as the liquid was clear a sample was withdrawn by means of the warmed pipette. By weighing the pipette full of solution, the quantity withdrawn as well as the density of the liquid was ascertained. A second sample was taken in like manner at the end of another hour. In most cases the samples were diluted to a known volume and titrated either with silver nitrate alone or (when hydrogen chloride was used) first with standardised alkali. In the case of potassium iodide, the contents of the pipette was washed into a tared, wide mouth, conical flask,

substances brought into competition exercised upon and within a given mass of water, the vehicle or medium within which the interchanges were effected being present in constant amount; emphasis is laid on this point, as the consideration is one which is commonly neglected, although probably it is the most important to bear in mind in dealing with mixed solutions.

Table I is given in illustration of the method followed in reducing the observations; the subsequent tables contain the actual data :—

Table I.—Solubility of Sodium Chloride.

	Water at 25° C			Dilute alcohol at 25° C. [1000 grammes of Water + 1 mol. Et(OH).]		
Sample.	A.	B.		Sample.	A.	B.
Density of saturated solution.	$d\frac{25}{25}$ 1·2015	1·2019		Density of saturated solution.	$d\frac{25}{25}$ 1·1794	1·1793
	grammes.	grammes.			grammes.	grammes.
Weight of saturated solution	12·0758	12·0015		Weight of saturated solution	11·8480	11·8368
Weight of salt found	3·2057	3·2100		Weight of salt found	2·9340	2·9300
Weight of water present	8·8701	8·8815		Weight of water + alcohol	8·9140	8·9068
				Weight of alcohol present (calculated)	0·3920	0·3917
				Weight of water present	8·5220	8·5151
Calculated from above, 100 grammes of water dissolve	36·14 sodium chloride.	36·14 sodium chloride.		Taking the value 36·14 grammes		
					grammes of water.	
				the salt saturates.......	8·1184	8·1073
				the alcohol controls....	0·4036	0·4078
				46 grammes alcohol control	47·36	47·81
				1 mol. alcohol controls	2·63	2·66
					molecules of water	

which was heated in an air oven kept at about 110°—120°; it was found possible, in this way, to prevent the salt from creeping up the side of the vessel.

In reducing the observations, the weight of salt present was deducted from that of the solution; the weight of hydrogen chloride or alcohol in the remaining liquid was then calculated and deducted, the remainder was the amount of water present. The weight of water required to form a saturated solution with the amount of salt present was then calculated and deducted from that of the water present; assuming that the remaining water was associated with the precipitant, its molecular ratio to the latter was then calculated. The graphs are drawn to represent the variation of the presumed state of hydration of the precipitant with the variation in the amount of the precipitant; they therefore serve to picture the dehydrating activity of the precipitant.

Table II.—Sodium Chloride.

Displacement of Salt by addition of Ethyl Alcohol to 1000 grammes of Water at 25° C.

Precipitant. Molecular proportion of alcohol per 55·5 mols. of water.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
	Weight of saturated solution taken.	$d\frac{25}{25}$.	Weight of salt present.	Weight of alcohol present.			
	grammes.		grammes.	grammes.	grammes.		
— {	A. 12·0758	1·2015	3·2057	nil	361·4	6·18	—
	B. 12·0915	1·2019	3·2100	nil	361·4	6·18	—
¼ {	A. 12·0192	1·1959	3·1303	0·1010	356·2	6·09	3·20
	B. 12·0020	1·1957	3·1275	0·1009	356·5	6·09	3·04
½ {	A. 11·9553	1·1899	3·0616	0·1999	352·2	6·02	2·84
	B. 11·9516	1·1896	3·0616	0·1998	352·3	6·02	2·80
1 {	A. 11·8480	1·1794	2·9340	0·3920	344·3	5·88	2·63
	B. 11·8368	1·1793	2·9300	0·3917	344·1	5·88	2·66
2 {	A. 11·6426	1·1592	2·7135	0·7522	331·8	5·67	2·27
	B. 11·6462	1·1593	2·7109	0·7528	331·3	5·66	2·31
5 {	A. 11·1688	1·1111	2·1642	1·6837	295·6	5·05	2·02
	B. 11·1656	1·1115	2·1602	1·6839	295·0	5·04	2·04

Table III.—Potassium Chloride.

Displacement of Salt by addition of Ethyl Alcohol to 1000 grammes of Water at 25° C.

Precipitant. Molecular proportion of alcohol per 55·5 mols. of water.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
	Weight of saturated solution taken.	$d\frac{25}{25}$.	Weight of salt present.	Weight of alcohol present.			
	grammes.		grammes.	grammes.	grammes.		
— {	A. 11·8600	1·1816	3·1676	nil	359·7	4·83	—
	B. 11·8561	1·1813	3·1376	nil	359·8	4·83	—
¼ {	A. 11·8196	1·1755	3·0621	0·0995	353·7	4·75	3·73
	B. 11·8060	1·1754	3·0611	0·0994	354·0	4·75	3·45
½ {	A. 11·7386	1·1687	2·9681	0·1971	346·2	4·64	4·2
	B. 11·7363	1·1689	2·9681	0·1971	346·3	4·64	4·1
1 {	A. 11·6073	1·1567	2·8051	0·3870	333·3	4·47	4·08
	B. 11·6178	1·1568	2·8138	0·3871	334·3	4·49	3·93
2 {	A. 11·4002	1·1353	2·5530	0·7453	315·1	4·23	3·44
	B. 11·4046	1·1357	2·5604	0·7451	316·1	4·24	3·37
5 {	A. 10·9018	1·0847	1·8943	1·6843	258·6	3·47	3·12
	B. 10·9012	1·0847	1·8977	1·6836	259·2	3·48	3·10

Table IV.—Ammonium Chloride.

Displacement of Salt by addition of Ethyl Alcohol to 1000 grammes of Water at 25° C.

Precipitant.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
Molecular proportion of alcohol per 55·5 mols. of water.	Weight of saturated solution taken.	$d\frac{25}{25}$.	Weight of salt present.	Weight of alcohol present.			
	grammes.		grammes.	grammes.	grammes.		
— {	A. 10·8494	1·0808	3·0719	nil	395·0	7·39	—
	B. 10·8456	1·0805	3·0719	nil	395·2	7·39	—
¼ {	A. 10·8244	1·0779	3·0468	0·0884	396·2	7·40	−0·64
	B. 10·8178	1·0780	3·0414	0·0884	395·6	7·40	−0·28
½ {	A. 10·8000	1·0753	2·9862	0·1756	390·9	7·31	1·16
	B. 10·7994	1·0753	2·9818	0·1757	390·2	7·29	1·38
1 {	A. 10·7542	1·0706	2·9051	0·3452	387·1	7·24	1·12
	B. 10·7682	1·0704	2·9074	0·3457	386·9	7·23	1·16
3 {	A. 10·5739	1·0528	2·6007	0·9668	371·1	6·94	1·12
	B. 10·5708	1·0528	2·6007	0·9665	371·3	6·94	1·11
5 {	A. 10·4192	1·0377	2·3537	1·5082	358·9	6·70	1·02
	B. 10·4202	1·0376	2·3519	1·5088	358·5	6·70	1·03

Table V.—Potassium Bromide.

Displacement of Salt by addition of Ethyl Alcohol to 1000 grammes of Water at 25° C.

Precipitant.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
Molecular proportion of alcohol per 55·5 mols. of water.	Weight of saturated solution.	Density of saturated solution, $d\frac{25}{25}$.	Weight of salt present.	Weight of alcohol present.			
	grammes.		grammes.	grammes.	grammes.		
— {	A. 13·8815	1·3830	5·6579	nil	688·0	5·78	—
	B. 13·8652	1·3824	5·6548	nil	688·7	5·79	—
¼ {	A. 13·7849	1·3725	5·5609	0·0935	683·9	5·75	1·40
	B. 13·7968	1·3727	5·5657	0·0936	683·9	5·75	1·40
½ {	A. 13·6846	1·3634	5·4111	0·1860	669·7	5·63	3·10
	B. 13·6864	1·3634	5·4110	0·1860	668·9	5·61	3·13
1 {	A. 13·4906	1·3445	5·1818	0·3654	652·3	5·48	2·90
	B. 13·5155	1·3443	5·1902	0·3661	652·1	5·48	2·92
3 {	A. 12·8715	1·2815·	4·4026	1·0269	591·5	4·97	2·60
	B. 12·8742	1·2815	4·4995	1·0277	590·8	4·97	2·62
5 {	A. 12·3792	1·2318	3·8232	1·5999	549·6	4·62	2·24
	B. 12·3773	1·2322	3·8261	1·5990	550·3	4·62	2·23

Table VI.—Potassium Iodide.

Displacement of Salt by addition of Ethyl Alcohol to 1000 grammes of Water at 25° C.

Precipitant.		Saturated solution.			Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
Molecular proportion of alcohol per 55·5 mols. of water.	Weight of saturated solution.	Density of saturated solution, $d\frac{25}{25}$.	Weight of salt present.	Weight of alcohol present.			
	grammes.		grammes.	grammes.	grammes.		
— { A.	17·3318	1·7273	—	—	—	—	—
B.	17·3565	1·7268	10·3802	nil	1487·9	8·96	—
¼ { A.	17·2382	1·7157	10·2440	0·0795	1481·5	8·92	0·97
B.	17·2387	1·7154	10·2440	0·0795	1481·4	8·92	0·97
½ { A.	17·1095	1·7036	10·0920	0·1578	1471·2	8·87	1·25
B.	17·1111	1·7042	10·0916	0·1578	1470·7	8·86	1·29
1 { A.	16·8938	1·6833	9·8122	0·3114	1449·3	8·73	1·47
B.	16·9156	1·6833	—	—	—	—	—
3 { A.	16·1388	1·6059	8·8498	0·8839	1381·6	8·32	1·32
B.	16·1244	1·6063	8·8535	0·8817	1385·7	8·33	1·27
5 { A.	15·4879	1·5425	8.0694	1·3872	1337·9	8·06	1·12
B.	15·4940	1·5420	8.0690	1·3885	1336·6	8·06	1·13

Table VII.—Ammonium Chloride.

Displacement of Salt by addition of HCl to 1000 grammes of Water at 25° C.

Precipitant.		Saturated solution.			Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt dissolved in 1000 grammes of water.	Apparent molecular hydration of precipitant.
Molecular proportion of hydrogen chloride per 55·5 mols. of water.	Weight of saturated solution used.	$\Delta\frac{25}{25}$.	Weight of salt present.	Weight of HCl present.			
	grammes.		grammes.	grammes.	grammes.		
— { A.	21·5398	1·0797	6·1154	—	396·48	7·41	—
B.	21·5380	1·0800	6·1154	—	396·52	7·41	—
¼ { A.	21·5674	1·0810	5·949	0·1446	385·1	7·19	6·33
B.	21·5276	1·0790	5·970	0·1437	384·7	7·18	6·61
½	21·5816	1·0815	5·7346	0·2835	368·48	6·88	7·85
1 { A.	21·6044	1·0827	5·3531	0·5783	341·5	6·38	} 7·75
B.	21·6020	1·0827	5·3435	0·5768	340·7	6·37	
5	21·9393	1·0992	2·4890	3·0255	174·24	3·25	6·9

Table VIII.—Sodium Chloride.

Displacement of Salt by addition of HCl to 1000 grammes of Water at 25° C.

Precipitant. Molecular proportion of hydrogen chloride per 55·5 mols. of water.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
	Weight of saturated solution used.	Δ 25/25.	Weight of salt present.	Weight of HCl present.			
	grammes.		grammes.	grammes.	grammes.		
— {	A. 23·9584	1·2012	6·3570	—	362·15	6·19	—
	B. 23·9810	1·2018	6·3760	—	362·33	6·19	—
¼ {	A. 23·8920	1·1972	6·0396	0·153	341·2	5·93	12·559
	B. 23·8862	1·1970	6·0253	0·154	340·2	5·92	12·601
½	23·7810	1·1915	5·8076	0·3175	328·93	5·62	10·19
1 {	A. 23·5816	1·1814	5·2600	0·6385	297·5	5·08	} 9·91
	B. 23·6174	1·1822	5·2674	0·6408	297·4	5·08	
5 {	A. 22·4010	1·1241	1·5841	3·2471	90·16	1·54	} 8·34
	B. 22·4218	1·1238	1·5776	3·2525	89·61	1·53	

Table IX.—Potassium Chloride.

Displacement of Salt by addition of HCl to 1000 grammes of Water at 25° C.

Precipitant. Molecular proportion of hydrogen chloride per 55·5 mols. of water.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
	Weight of saturated solution used.	Δ 25/25.	Weight of salt present.	Weight of HCl present.			
	grammes.		grammes.	grammes.	grammes.		
— {	A. 23·5746	1·1810	6·2297	—	360·83	4·84	—
	B. 23·5952	1·1811	6·2407	—	359·60	4·82	—
¼ {	A. 23·4750	1·1766	5·907	0·159	338·6	4·54	12·99
	B. 23·4370	1·1764	5·899	0·157	339·33	4·548	13·02
½	23·3786	1·1742	5·6321	0·0770	323·15	4·33	11·42
1 {	A. 23·1776	1·1617	5·0551	0·6397	289·2	3·87	} 11·03
	B. 23·1592	1·1611	5·0350	0·6485	288·1	3·86	
3 {	A. 22·5708	1·1320	3·023	1·9218	171·51	2·29	9·74
	B. 22·5800	1·1326	3·040	1·9206	172·50	2·31	9·68
5 {	A. 22·3344	1·1184	1·5134	3·2392	86·07	1·02	} 8·42
	B. 22·3244	1·1184	1·5477	3·2169	88·14	1·18	

If the apparent dehydrating power of the precipitant be taken as the measure of its activity in competition with the dissolved salt, it will be obvious, on reference to Diagram 1 (below), in the first place, that although alcohol is less active than hydrogen chloride, the same kind of influence is exercised by both precipitants, as the two sets of graphs correspond in most respects.

DIAGRAM 1.
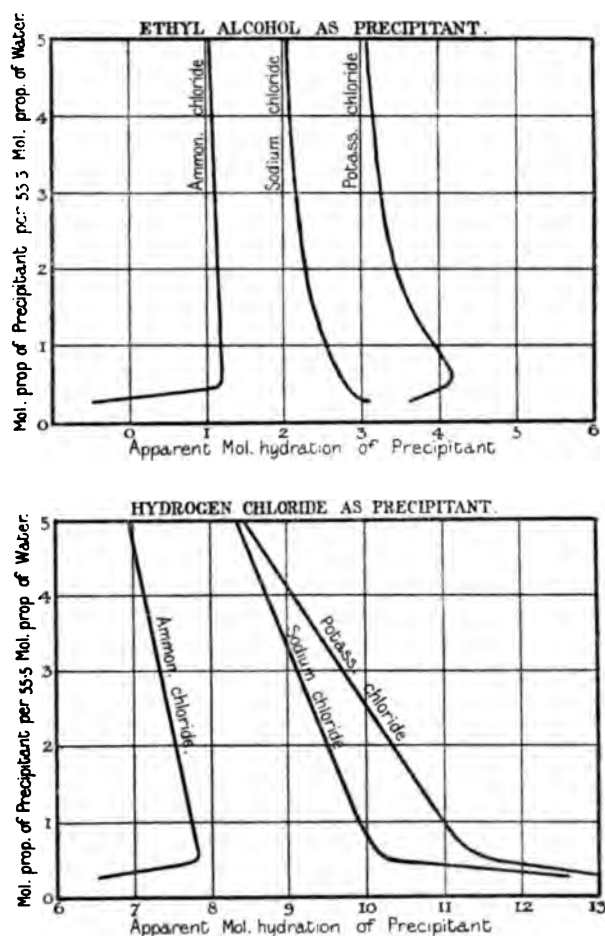
It is important to consider Engel's results, and especially his conclusions, in connection with our determinations; as his observations were made at 0°. they afford data for a comparison of the effects produced at 0° and 25°. Engel did not adequately take into account the proportion of water present, but assumed that the phenomena would be the same if considered with reference

to a constant amount of water;* when his observations are recalculated from
our point of view (Table I) and the results are expressed by graphs, it is
obvious that they correspond very closely with our own (Diagram 2).

DIAGRAM 2.

Apparent Molecular hydration of Precipitant.
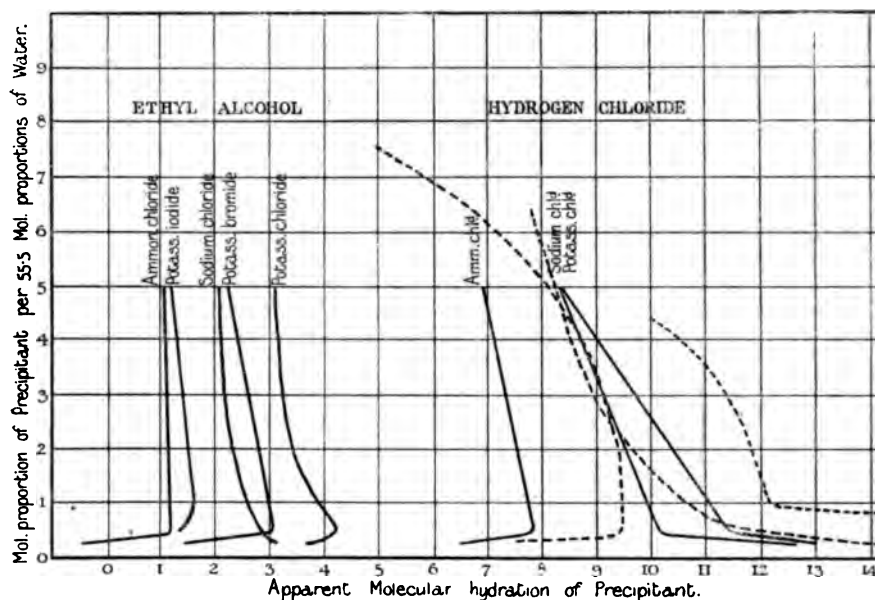
The graphs afford a most interesting picture of the state of the salts in
solution at various stages. As the precipitant has the largest effect when
present in least amount, it is clear that the condition of the salts in highly
concentrated solutions is peculiar and different from that which they assume
in presence of a considerable proportion of the precipitant: sodium and
potassium chlorides both exist in an eminently precipitable form in the

* His statement on this point is as follows :—

6. Tant que le chlorure est précipité équivalent à équivalent par l'acide chlorhydrique,
la quantité d'eau contenue dans un même volume de la solution du chlorure en présence de
quantités variables d'acide est sensiblement constante. Il en résulte que le phéromène
reste le même si l'on rapporte à un même poids d'eau la quantité de chlorure en solution
en présence de quantités variables d'acide chlorhydrique.

7. L'acide chlorhydrique n'agit pas en fixant de l'eau et empêchant ainsi celle-ci d'agir
comme dissolvant sur le chlorure. La quantité d'eau laissée libre par la précipitation
d'un équivalent du sel varie, en effet, dans chaque cas, et, par suite, l'acide chlorhydrique
s'opposerait à la dissolution de chaque chlorure en s'unissant lui-même à une quantité
d'eau variable dans chaque cas et sensiblement égale à celle qu'exige, pour se dissoudre, un
équivalent du chlorure considéré.

8. Enfin, l'eau qui se combine avec l'acide chlorhydrique et l'eau de cristallisation du
chlorure semblent intervenir comme dissolvant, au même titre que le reste de l'eau,

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concentrated solutions, water being held by them far less firmly than it is subsequently; ammonium chloride, on the other hand, is present in a form in which at first it is more soluble in the mixed solvent than in water.

As ammonium chloride is readily volatilised and, when vaporised, has a density corresponding to the formula NH_4Cl, it may be assumed that it enters into and exists in solution at least largely in the monadic form; but in concentrated solutions, in which, probably, there is not sufficient water to hydrate all the molecules, a considerable proportion of the monads are unhydrated and capable of combining with substances such as hydrogen chloride and alcohol. As the amount of precipitant is increased, the amount of salt in solution is diminished and a proportion is soon reached which permits of the hydration of most, if not all, of the salt molecules. Ere this stage is reached, however, the proportion of hydrogen chloride molecules present becomes sufficiently large once more to exert a solvent action on the salt, which, in consequence, is thrown out of solution in a diminishing proportion.

It can scarcely be doubted that the easily precipitable form of potassium and sodium chlorides is a complex, polymerised molecule, closely related, perhaps, to the solid form: in fact, the solution may be regarded as saturated

puisque le phénomène est le même pour les chlorures anhydres et pour les chlorures qui cristallisent avec de l'eau de cristallisation.

Engel's data for ammonium chloride are given by way of example in the following table, together with (in the last two columns) the corrected values we have calculated from them on the assumption that water is present in constant amount throughout.

Quantité de chlorure d'ammonium dans 10 c.c. de solution *saturée en présence de quantités variables d'acide chlorhydrique.*

—	NH₄Cl.	HCl.	Comme des équivalents.	Densité.	Eau.	Molecular proportion of HCl in 1000 grammes of water.	Molecular hydrate value.
						grammes.	
I	46·125	0	46·125	1·076	8·29	—	—
II	43·6	2·9	46·5	1·069	8·25	0·351	7·49
III	41·0	5·5	46·5	1·070	8·31	0·661	9·477
IV	39·15	7·85	47·0	1·071	8·33	0·912	9·05
V	36·45	10·85	47·30	1·093	8·39	1·29	9·43
VI	27·37	21·4	48·7	1·078	8·53	2·50	9·29
VII	10·875	53·0	63·875	1·106	8·54	6·21	6·88
VIII	8·8	61·0	69·8	1·114	8·12	7·51	4·96

Calculated from data given in table—

with the solid with which it is in equilibrium. Comparison of the observations at 0° and 25° seems to show that this " solid form " persists in presence of a larger proportion of the precipitant at 0° than it does at 25°, at least a molecular proportion of hydrogen chloride being required to destroy it at 0° and only about half as much at 25°. Moreover, to judge from the shortness of the horizontal branches of the sodium and potassium chloride graphs at 0° in comparison with those at 25°, it would seem that at the higher temperature these chlorides are also to some extent present as unhydrated monads soluble in the precipitant.

In the case of ammonium chloride, the increased solubility is noticeable at 0° at a somewhat "higher level" than at 25°, probably because the more soluble chloride $NH_4Cl : ClH$ is more stable at the lower temperature.

It will be seen that in the case of ammonium and potassium chloride the 0° graphs curve more and more to the left as the concentration of the hydrogen chloride is increased; no such marked trend is noticeable at 25°. It is to be supposed that the difference arises from the instability of the double chlorides at the higher temperature in competition with water. The fact that the alcohol graphs resemble the 25° hydrogen chloride graphs affords support to this view, as it is to be expected that alcohol would have but little chance in competition with water.

From the ionic dissociation point of view, dissociation should be repressed as the amount of hydrogen chloride is increased: therefore, instead of increasing, the solubility should diminish proportionally as the concentration of the hydrogen chloride is increased.

It will be observed that the behaviour of potassium bromide and iodide in presence of alcohol is similar to that of the chloride and that the greater the molecular solubility of the salt the more closely it approximates to ammonium chloride; probably the proportion of monads in the concentrated solution is larger in the case of the more soluble salt, which also has the lower melting point (Diagram 3).*

Except, perhaps, in the case of ammonium chloride, the greater proportionate solubility of the salts in. regions represented by the upper portion of the diagram, as well as the lower state of hydration of the precipitant which is indicated by the backward slope of the graphs, can only in part be ascribed to the formation of a soluble compound with the precipitant; probably it is mainly due to the production of the more soluble monads in increasing

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* It is perhaps appropriately suggested here that probably the great increase in molecular solubility of ammonium chloride (from about 6 to 13·5 proportions per 1000 grammes of water) between 0° and 100° is to be correlated with the low melting point of the salt.

proportion as the number of interposed molecules of the precipitant is increased. The same kind of effect is reciprocally exercised by two salts such as potassium and sodium chloride, a saturated solution containing per 1000 molecules of water of the former 88 and of the latter 111 molecular proportions, whilst a solution saturated with both salts contains 39 of the former to 89 of the latter: or, in sum, 128, an excess of $128 - 111 = 17$ monadic proportions over the number contained in a saturated solution of the more soluble salt. The monads of the two salts evidently interfere with one another's freedom of combination: consequently, the mixed solution contains, in the aggregate, a greater number of molecules than can coexist in the

DIAGRAM 3.
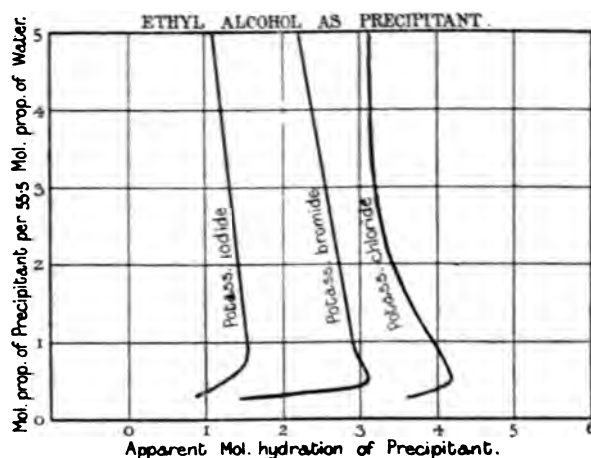
solution of the more soluble salt; evidence in support of this view is to be found in the fact that the solution of the mixed salt has a lower vapour pressure (16·84 mm.) than has the solution of sodium chloride (17·7) or that of potassium chloride (19·2). In the mixed solution, at 25°, the more soluble sodium chloride is present in a proportion somewhat larger than that corresponding to its solubility in comparison with the solubility of potassium chloride; evidently, therefore, it is able to compete somewhat more successfully for the water. This preponderance of the more soluble salt is even more obvious in cases in which the competition is with a salt which is but moderately soluble and which, therefore, presumably has but a slight hold upon the water—for example, whereas potassium chloride and sulphate are present in their saturated solutions in the relative molecular proportions of 88 to 12, a solution saturated with both salts contains to 84 of the former only 1·5 molecular proportions of the latter, and its vapour pressure (19 mm.) is

but slightly less than that of chloride alone (19·2). The solubility of sodium chloride in the presence of potassium chloride, it is well known, diminishes slightly between 0° and 100°; this is probably due to the diminution in its affinity for water as the temperature rises and the concomitant increase in the tendency to reform complex molecules—the decomposition of which at lower temperatures must be regarded as determined largely by the affinity of water for the monads. At 100° potassium and sodium chlorides are almost equally soluble (4·4 : 4·6 molecular proportions), the former having the advantage—probably because it can hold water more firmly.

The distinction between monadic and polymerised molecules has been almost left out of account by those who have attempted to apply the ionic dissociation hypothesis to the discussion of solubility. It is clearly necessary, however, to acknowledge the existence in solutions of a great variety of molecular conditions simultaneously : of monadic and polymerised molecules both in the anhydrous and hydrated states and, in some cases, of compounds formed by the association of the admixed solutes ; and also to recognise that the solvent itself as well as the dissolved substances is in a state of continued flux. The interplay of these conflicting and competing elements is sufficient, probably, to account for all the varied phenomena afforded by solutions without the introduction of hypothetical considerations based on the presumed occurrence of dissociation into independent ions. And even if, on other grounds, it were necessary to postulate the occurrence of ionic dissociation in solution, the phenomena are clearly of so complicated a character that it is impossible to apply such an interpretation without introducing the many other considerations which obviously demand attention. The variables are so numerous that it may be doubted whether it will ever be possible to develop any simple treatment of solutions.

III. *The Sucroclastic Action of Nitric Acid as influenced by Nitrates.* By R. WHYMPER, Salters' Company's Research Fellow, City and Guilds of London Institute, Central Technical College.

The experiments carried out by R. J. Caldwell on the hydrolysis of cane sugar by chlorhydric acid in presence of various chlorides, described in the first of these studies,* have afforded a means of judging of the extent to which such salts exercise a concentrating effect and of determining the average degree of hydration of the chlorides in solution. In the present

* 'Roy. Soc. Proc.,' 1906, A, vol. 78, p. 272.

communication it will be shown that the method is equally applicable to nitrates and that these are nearly as fully hydrated in solution as are the corresponding chlorides—a conclusion of some interest, as nitrates are not usually credited with any considerable dehydrating power.

My observations have been made with the apparatus* which was used by Caldwell and in the manner described by him: throughout the enquiry I have also enjoyed the advantage of his experience and have to thank him for the advice which he has given me.

The salts examined were recrystallised until neutral, the ammonium nitrate from alcohol. The acid used in preparing the solutions was approximately twice normal: it was titrated against calcite and also against a solution of baryta standardised by another worker.

The solution to be examined was filtered into the polarimeter tube at as near to 25° as possible and the tube was then placed in position in the heated jacket attached to the instrument. To give time for the liquid to acquire the temperature of the thermostat, it was found to be advisable to wait before taking the initial reading until about 20 minutes later, when the rotatory power was about 10° to 11°: by operating in this manner, the error due to initial disturbances is avoided. Mean time readings were taken at 30, 35 . . . . . . 100 minutes after the first: a final reading was taken to determine the end point at least 24 hours later, when the action was practically at an end. Each reading reported represents the mean of five readings taken at minute and half minute intervals on either side of the mean time.

The results obtained in two complete experiments entirely representative of the series are recorded in Tables I and II. It will be noticed that the 30-minutes values are both high: this is almost uniformly the case and appears to be due to the fact that the eye was less sensitive just after coming into the dark room than it was subsequently. The thermometers attached to the jacket were watched throughout the experiment and it was usually possible to correlate marked changes in the value of the constant with any unusual variation of the temperature. An illustration of this fact is given in Table I: it will be seen that the value of K at 35 minutes is given as 12 units above the mean value; a fall in temperature of about 0°·1 was noticed when the reading was taken at this time.

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* To adjust the rate of flow of the water through the jacket of the polarimeter tube, the water was passed through a tube in which a glass rod, of nearly the same diameter, could be moved up and down ; this tube was provided with inlet and exit tubes and the water passed through the interval between the rod and the main tube. By shifting the rod, the rate of flow of the water could be adjusted far more delicately than by means of the ordinary screw clip arrangement.

Table I. ½ gramme-molecule of Cane Sugar + 1 gramme-molecule of HNO₃ + 1 gramme-molecule of LiNO₃ + 1000 grammes of H₂O + 13H₂O.

t	$\frac{a}{H}$	$a-x$	$K\left(\frac{10^y}{t}\log\frac{a}{a-x}\right)$
0	9·444	14·766	—
30	8·88	10·688	466
45	4·788	10·080	475
60	4·888	9·066	460
75	8·8	9·188	463
90	8·888	8·000	463
105	2·888	8·810	463
120	2·417	7·76	467
135	2·088	7·800	465
150	1·887	7·0	463
165	1·888	6·000	461
180	0·887	6·8	462
195	0·88	6·088	462
210	0·888	6·088	462
225	0·411	6·88	464
1000	−0·2	6·188	459
∞	−8·888		

Mean 463

Table II. ½ gramme-molecule of Cane Sugar + 1 gramme-molecule of HNO₃ + 1 gramme-molecule of AgNO₃ + 1000 grammes of Water.

t	$\frac{a}{H}$	$a-x$	$K\left(\frac{10^y}{t}\log\frac{a}{a-x}\right)$
			54
			54
			33
			58
			58
			58
			58
			58
			58
			58
			33
			57
			57

Mean 54

Table III.—⅓ gramme-molecule of Cane Sugar + 1 gramme-molecule of HNO₃ + 1 gramme-molecule of Salt + 1000 grammes of Water + X gramme-molecules of Water.

Salt.	Volume of solution.	$K\left(\dfrac{10^5}{t}\log\dfrac{a}{a-x}\right).$	X (gramme-molecules).	K.	Average hydrate.
Sugar alone ...	c.c. 1136·4 1136·6 1137·1	463 467 466			·
		Mean 465			
AgNO₃	1173·3	531			
			20H₂O	339	
			9H₂O	429	
			6H₂O	459	
			5H₂O	{ 465 466	5H₂O.
NH₄NO₃	1167·9	570			
			10H₂O	444	
			7H₂O	{ 466 466	7H₂O.
KNO₃	1180·1	566			
			10H₂O	453	
			8H₂O	{ 462 465	8H₂O.
NaNO₃	1172·1	607			
			20H₂O	373	
			12H₂O	444	
			11H₂O	{ 464 466	11H₂O.
LiNO₃	1179·3	578			
			7H₂O	488	
			10H₂O	478	
			11·5H₂O	477	
			13H₂O	463	13H₂O.
			15H₂O	432	
Sr(NO₃)₂	1197·9	733			
			23H₂O	420	
			20H₂O	443	
			18H₂O	{ 463 463	18H₂O.

The results call for little remark, as the hydration values arrived at, given in the last column of the table, seem to be entirely rational. It is difficult to avoid the conclusion that they dispose of the contention that nitrates exist in solution unhydrated.

IV. *The Hydrolysis of Methylic Acetate in Presence of Salts.* By H. E. Armstrong, F.R.S., and J. A. Watson.

In principle, the method developed in the first of these studies of determining the average "concentrating effect" of a salt on the activity of an acid hydrolyst is applicable to all cases of hydrolysis other than those

induced by enzymes; moreover, the results obtained with chlorides and nitrates with cane sugar are so entirely rational that there can be little doubt that it is valid generally as a means of determining the average degree of hydration of a salt in solution. But as the substances in a solution share the solvent and are in competition, it is to be expected that hydration values will be found to vary from case to case and that it will not always be possible to approximate to the true hydrating effect of a salt: indeed, cases are known in which salts apparently retard hydrolysis.

To determine the limitations of the method, therefore, it is necessary to investigate the behaviour of hydrolytes other than cane sugar. That chosen for the experiments referred to in this account was the ethereal salt *methylic acetate*, $CH_3.CO.OCH_3$. This substance is entirely different in constitution from cane sugar and is present in solution, presumably, in the form of simple molecules which are hydrated to but a very slight extent, whilst cane sugar doubtless exists in solution more or less in the form of associated complex molecules and in a moderately hydrated condition—perhaps as a "hexhydrate" at least. Presumably, therefore, the system consisting of water, chlorhydric acid and cane sugar contains less " free water " than the equivalent system in which methylic acetate takes the place of sugar: a salt dissolved in the latter system should, at least in concentrated solutions, therefore have a greater chance of becoming hydrated than it would have if dissolved in the former. From this point of view it was to be expected that the hydration values deduced with the aid of methylic acetate, if not coincident with those determined by means of cane sugar, would be higher; as a matter of fact, lower values are obtained.

The average degree of molecular hydration arrived at with the aid of the two hydrolytes is as follows:—

—	Hydrolysis by chlorhydric acid.		—	Hydrolysis by nitric acid.	
	Sugar.	Acetate.		Sugar.	Acetate.
—	—	—	Silver nitrate ...	5	
Ammonium chloride ...	10	5	Ammonium ,, ...	7	−2
Potassium ,, ...	10	8	Potassium ,, ...	8	1
Sodium ,, ...	13	10	Sodium ,, ...	11	3
Lithium ,, ...	—	—	Lithium ,, ...	13	
Barium ,, ...	19	18	Barium ,, ...		
Strontium ,, ...	—	—	Strontium ,, ...	18	+ 5 (?)
Calcium ,, ...	22	20	Calcium ,, ...	—	.7

The results are very remarkable—evidently some special influence comes

into play, particularly in the case of the nitrates. It is not difficult to diagnose the character of this influence.

It has been shown by Arrhenius[*] and by Spohr[†] that chlorides and nitrates, but not sulphates, exert a slight retarding effect on the hydrolysis of ethylic acetate by alkali: therefore it is probable that a similar retarding influence comes into play when hydrolysis is effected by an acid and that this to some extent masks and counteracts the proper accelerating effect of the salt. Probably the effective hydrolyst is the hydrated acid: assuming, however, for the sake of simplicity, that water acts alone, the hydrolysis of the ethereal salt doubtless involves the association of the two molecules and subsequent partition of the complex into acid and alcohol, thus—

$$CH_3.COOMe + OH_2 \longrightarrow CH_3.C\overset{\displaystyle OH}{\underset{\displaystyle OMe}{H}} \longrightarrow CH_3.COOH + HOMe.$$
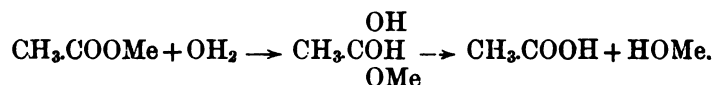
A simple explanation is afforded of the interference of a salt and of the diminished acceleration or retardation observed in the case of methylic acetate, if it be assumed that the salts ($M'X'$) also enter into association with the ethereal salt—

$$CH_3.COOMe + M'X' \longrightarrow CH_3.C\overset{\displaystyle X}{\underset{\displaystyle OMe}{H}}$$
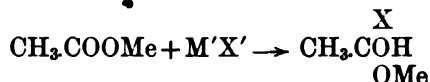
and that consequently they hinder to some extent the association of ethereal salt and hydrolyst.[‡] The keto-group, CO, is so generally admitted to be unsaturated and capable of combining with compounds of the form $R'X'$ that such an explanation cannot be regarded as otherwise than simple and rational. We are not aware, however, that it has been suspected up to the present time that nitrates are peculiarly active in thus combining.

Results such as we have described are altogether irreconcilable with the tenets of those who accept the doctrine of ionic dissociation. They serve, however, to explain the results obtained on hydrolysing ethereal salts with alkali in presence of metallic salts, and we venture to think that it is no

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* 'Zeit. Phys. Chem.,' vol. 1, p. 1107. According to Arrhenius, the effect on the rate of hydrolysis by sodic hydrate of the corresponding salts is greater than that exercised by the potassium salts on the activity of potassic hydrate. Potassium iodide has a greater influence than the bromide, which in turn is more active than the chloride. Arrhenius speaks of the retardation as a perturbation of the second order, due to forces the true nature of which will not be easily determined.

† *Ibid.,* vol. 2, p. 194.

‡ In the case of hydrolysis by alkali, the experiments have been made with quite dilute solutions, between limits within which concentration has but little influence, so that the concentrating effect of the salt cannot well become apparent merely as a diminished acceleration and there is consequently an actual retardation.

longer necessary to associate any element of mystery with such hydrolytic phenomena; the long recognised conventional articles of belief of the chemist afford a sufficient and satisfactory explanation of the observed departures from uniformity.

The hydrolysis of methylic acetate by acids was first investigated systematically by Ostwald in 1883 and developed by him into a method of appraising the relative activity of acids. Trey, at Ostwald's instigation, shortly afterwards studied the effect of several neutral salts on the action of the corresponding acids and showed that they exercised an accelerating influence; as Trey's and all subsequent experiments, however, were made with volume-normal solutions, it has remained uncertain to the present time whether or to what extent the increased activity of the acid is due to the mere displacement of water by the salt. It was, therefore, desirable to institute experiments in which the water was no longer a variable, so that the specific influence of the salt might be ascertained and its degree of hydration determined, following the plan developed in Part I of these studies.

The solutions we have used contained, as a rule, 1000 grammes of water, ½ gramme-molecular proportion of methylic acetate and 1 gramme-molecular proportion of hydrogen chloride or nitric acid; when a salt was added, 1 gramme-molecular proportion was always used.

In carrying out the experiments, 100 c.c. of twice weight-normal acid (chlorhydric or nitric) was introduced into a Jena flask and when the temperature of the liquid was 25° a like quantity of a weight-normal solution of methylic acetate, also at 25°, was quickly added; the two solutions having been mixed, 10 c.c. were promptly withdrawn and run into 10 c.c. of a solution of twice normal sodic acetate, the time being noted; the flask containing the main bulk of the solution was forthwith placed in the thermostat, which was carefully kept at 25°. Samples were withdrawn every 10 minutes up to two hours from the commencement of the experiment. The end point was determined the next morning. An important improvement was effected by using the sodic acetate to check the action of the strong acid. The titrations were made with N/5 baryta, using phenolphthalein as indicator.

When salts were added, the weighed quantity of salt was dissolved in the acid solution before the solution of methylic acetate was run in. In some cases, in order to dissolve the necessary amount of salt, 50 c.c. of water were added to the acid and the solution of methylic acetate was made of double strength. The first reading was taken only after 30 minutes from the commencement of the experiment.

Two complete series of observations are given in Table I.

Table I.

Composition of Solution—
14·92 grammes KCl.
100 o.c. 2N/HCl.
100 o.c. N/MeĀc.

KCl.8H₂O—
14·92 grammes KCl.
100 c.c. HCl.
100 c.o. MeĀc.
28·82 o.c. water.

Time.	Titration.	$a-x$.	$\frac{10^5}{t}\log\frac{a}{a-x}$.	Time.	Titration.	$a-x$.	$\frac{10^5}{t}\log\frac{a}{a-x}$.
	c.c.				c.c.		
0	52·3	23·3	—	0	45·9	21·3	—
30	57·4	18·2	*357**	30	49·9	17·3	301
40	58·5	17·1	336	40	51·2	16·0	*310*
50	59·7	15·9	332	50	52·2	15·0	304
60	60·9	14·7	333	60	53·25	13·95	306
70	62·2	13·4	342	70	54·2	13·0	306
80	63·1	12·5	338	80	55·05	12·15	305
90	64·1	11·5	340	90	55·9	11·3	305
100	65·05	10·55	344	100	56·7	10·5	307
110	65·7	9·9	337	110	57·4	9·8	306
End point	75·6	Mean...	338	End point	67·2	Mean...	305

* The values entered in *italics* were neglected.

The following (Table II) are the values of the velocity constant obtained with acetate alone or with salt present in the solution and those on which the determinations of the hydration values are based.

It will be noticed that the values are not as accordant as those determined with the aid of the polarimeter, but this was only to be expected, as the possibility of error is so much greater, owing to the numerous measurements to be made with pipettes and the difficulty of taking samples at exactly the right times, as well as of checking the action; moreover, titration is not nearly so accurate a process as the estimation of optical activity.

Table II.

MeÅ + HCl		+ KCl.	KCl.8H₂O.		+ NaCl.	NaCl.10H₂O.		+ NH₄Cl.	NH₄Cl.5H₂O.	
303	291	357	301	318	385	299	292	313	301	310
296	300	336	310	316	359	300	296	276	290	300
303	300	332	304	294	341	305	313	314	307	301
290	312	383	306	303	361	316	302	321	322	305
307	308	342	306	295	360	309	299	816	307	310
304	310	338	305	301	361	302	303	325	310	309
301	303	340	305	297	361	314	298	329	310	—
—	305	344	307	303	360	—	301	—	316	—
—	308	337	306	—		—	301			
302	304	338	305	303	360	303	301	320	306	306
	303			304			302			306

BaCl₂.18H₂O.			+ CaCl₂.	CaCl₂.20H₂O.	MeÅ + HNO₃.		+ KNO₃.	KNO₃.H₂O.	+ NaNO₃.
304	297	307	420	292	281	234	265	289	268
311	312	316	418	304	298	270	282	284	279
318	311	306	428	304	266	278	284	273	290
314	307	311	421	305	284	283	284	274	294
314	291	307	430	302	276	279	280	275	290
301	310	313	429	299	272	279	285	269	290
298	304	309	—	299	278	272	286	277	284
—	295	302	—	299	277	282	—	276	—
—	307	—			—	282	—	—	
309	304	308	424	300	273	278	283	277	290
	307					278		277	

NaNO₃.3H₂O.	NH₄NO₃.	NH₄NO₃—2H₂O.	+ LiNO₃.	Ca(NO₂)₂.7H₂O.
291	254	242	257	260
274	245	2.0	267	277
270	256	273	276	274
272	274	279	278	272
273	261	278	277	274
277	266	269	280	277
272	268	273	277	276
				274
				278
273	263	275	278	275

The results obtained are summarised in the following Table III :—

Table III.—Rate of Hydrolysis of Methylic Acetate by Chlorhydric and
Nitric Acids in Solutions of different Compositions.

Composition of solution.	$\dfrac{10^5}{t} \log \dfrac{a}{a-x}.$	Amount of water added.
		gramme-molecules.
0·991 N/HCl + N/MeĀc	303	
+ N/2 MeĀc	294	
	294	
+ N/4 MeĀc	282	
+ N/2 MeĀc + N/2MeOH	292	
	293	
	294	
+ N/2CH₃CO₂H	311	
	316	
N/HCl + N/2 MeĀc	302	
	304	
+ KCl, 1 gramme-molecule	338	
	290	9
	305 } 303 }	8
+ NaCl, 1 gramme-molecule............	360	
	287	12
	303	
	301	10
+ NH₄Cl, 1 gramme-molecule	320	
	306 } 306 }	5
+ CaCl₂, 1 gramme-molecule	424	
	300	20
+ BaCl₂, 1 gramme-molecule	320	10
	309 } 304 } 308 }	18
N/HNO₃ + N/2 MeAc	278	
	278	
+ KNO₃, 1 gramme-molecule	283	
	277	1
+ NaNO₃, 1 gramme-molecule..........	290	
	273	3
+ LiNO₃. 1 gramme-molecule	278	
+ NH₄NO₃, 1 gramme-molecule	263	
Less 2 gramme-molecules of water	275	−2

Although, as hydrolysis proceeds, both methylic alcohol and acetic acid
are formed and accumulate in solution, the results afford no evidence that
they influence the rate of change. The effect of these substances when
added in advance is different, methylic alcohol being apparently without
action, whilst acetic acid has a distinct accelerating influence*—as it has
in the hydrolysis of cane sugar. That the alcohol has no influence is

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* It has practically no hydrolytic effect *per se* during the time occupied in carrying out
an experiment.

somewhat surprising in view of the fact that ethylic alcohol retards the hydrolysis of cane sugar to a not inconsiderable extent; this difference between the two cases is, perhaps, significant and deserving of further study. Apparently, the concentrating effect which the methylic alcohol may be supposed to exercise is just balanced by the extent to which it acts in neutralising acid; on the other hand, it would seem that the acid alcoholate is not much less active than the acid hydrate, although in the case of cane sugar it is relatively ineffective. The effect of increasing the concentration of the ethereal salt appears to be very similar to that observed in the case of cane sugar.

It is proposed to extend the experiments to other ethereal salts.

V. *The Discrimination of Hydrates in Solution.* By H. E. ARMSTRONG, F.R.S., and R. J. CALDWELL, B.Sc., Leathersellers' Company's Research Fellow, City and Guilds of London Institute, Central Technical College.

There are many signs that the uncertainty which has so long attended the interpretation of the peculiarities manifest in solutions may be dispelled at no distant date and a common understanding arrived at, as the old belief in the existence of hydrates is once more coming to the front[*] and there is a growing tendency to admit that the phenomena are more complex than is commonly supposed.

Inasmuch as there are no arguments from the chemical side which either compel or even require belief in ions as independent entities and not a few incompatible with such an assumption, which support the view that association[†]—not dissociation—is the precedent of chemical interchange, physicists may well be challenged to reconsider the grounds on which they are led to suppose that ionic dissociation takes place in solution: the cogency of their arguments has been frequently questioned from the chemical side without the objections being met.

To state the case briefly: apart from the fact that it is irrational and inapplicable to compounds generally (only to electrolytes), three main lines of argument appear to militate directly against the assumptions postulated by the advocates of the ionic dissociation hypothesis.

1. The complex sugars and ethereal compounds generally are hydrolysed by all acids; and these latter differ only in the degree of activity which they

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[*] Comp. Nernst, 'Zeits. phys. Chem.,' 1889, vol. 4, p. 372; 'Centralblatt,' 1900, vol. 2, p. 620.

[†] Comp. E. Fischer, 'Deut. chem. Ges. Ber.,' 1907, vol. 40, p. 495.

manifest towards the various hydrolytes. Enzymes, on the other hand, act selectively. The strength of the case which this argument affords is probably in no way realised by those who are not fully conversant with the phenomena. It is assumed by the ionic dissociation school that the action of acids is exercised by the free hydrogen ions and that the activity of the acid is proportional to the extent to which the acid is dissociated in solution into positive and negative ions. But as enzymes do not behave as electrolytes in solution, although extraordinarily active in comparison with acids, some other explanation must be found to account for their activity as hydrolysts. The proof that the enzyme enters into association with the hydrolyte appears to be complete* and as there is reason to believe that acids also combine transiently with ethereal compounds, there seems to be no reason why an explanation should be given of their action which is inapplicable to enzymes.

2. From the ionic dissociation standpoint, the dissociation of an acid into free ions should be repressed by a neutral salt containing the negative ion of the acid; consequently, when present together with the acid, as the salt is inert *per se*, the salt should diminish the activity of the acid: in point of fact, it increases it. As non-electrolytes sometimes exercise an accelerating influence similar to that of salts, although to a less extent, there is again no reason to attribute altogether special properties to electrolytes and to account for their activity by an explanation which cannot be applied to non-electrolytes.†

3. This same argument may be applied to the precipitation of salts from solution, as non-electrolytes are active as well as electrolytes.‡

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* 'Roy. Soc. Proc.,' B, 1907, vol. 79, p. 360.

† An argument to the same effect may be based upon the fact that hydrogen chloride, calcium chloride and alcohol produce similar effects in altering the absorption spectrum of cobalt salts (Hartley, Royal Irish Academy, 1900, II, vol. 7, p. 253).

‡ In tracing the development of the theory of electrolytic dissociation, in a lecture which he gave at the Royal Institution on June 3, 1904 ('Proceedings of the Royal Institution,' vol. 17, p. 552), Arrhenius laid stress on the fact that in the case of permanganic acid and its various metallic salts, as well as in the case of the salts of pararosaniline with acids, the absorption spectrum does not vary from salt to salt except in intensity, whereas the spectrum of fluorescein is modified by the smallest chemical change of the molecule : he advances the explanation that the uniform behaviour of permanganates and of rosaniline salts is due to the fact that the spectra are all produced by the dissociated permanganate ion in the one case and by the rosaniline ion in the other. Those who have made use of this argument have paid little attention to what is known of the relation of colour to structure : it is well established, in the case of fluorescein, that the action of alkali extends beyond the formation of a salt and involves the formation of an isodynamic compound of entirely different structure and very differently coloured ; no such change of structure is involved in the formation of the permanganates and of the ordinary rosaniline salts. In the case of rosaniline it is possible, by varying the proportions of acid, to produce salts of different structure, in which case the colour

The one respect in which electrolytes and non-electrolytes undoubtedly differ is in their affinity for water—which appears to enter into combination with the former in some particularly intimate manner ; it is reasonable to suppose that their special behaviour towards an electric current is conditioned by this peculiarity. From this point of view, the study of the phenomena of hydration is of exceptional importance.

It appears to be now so widely admitted that hydrates are formed in solution that it is unnecessary to discuss the subject from the general point of view ; the question to be decided is rather what particular hydrates are present. Passing over evidence such as has been adduced by Mendeleeff, Pickering, Hartley and others, the recent work of Harry C. Jones may be specially referred to, as he has brought forward a large amount of what purports to be new experimental evidence bearing on the determination of the extent to which salts are hydrated in solution.*

also varies. The argument from colour, far from supporting the dissociation hypothesis, in reality is opposed to it.

* The values which this observer arrives at are in many cases so remarkable that his methods appear to be more than open to doubt. Thus he considers that sodium, potassium and ammonium chlorides have little, if any, attraction for water and that the nitrates are even less hydrated than the corresponding chlorides. Magnesium and other sulphates give abnormal results ; this salt "appears to form no hydrates in aqueous solution, notwithstanding that it crystallises with 7 molecules of water . . . it has considerable hydrating power, but this is masked by the large amount of polymerisation which the sulphates undergo." As the concentration is increased, the degree of hydration of caustic soda falls to zero and then rises. And whilst ammonium hydroxide is regarded as being as highly hydrated as caustic soda and potash, the mineral acids are uniformly represented as anhydrous in dilute and hydrated in concentrated solutions.

The method adopted by Jones on which these conclusions are based involves, in principle, the assumption that the number of units—whether ions or molecules—in solution can be deduced directly from observations of the electrical conductivity ; it also involves the assumption that this value can be deduced equally well from the depression of the freezing point even in concentrated solutions made on the volume-normal plan. In cases in which the two values differ, the difference is attributed to the formation of a hydrate and the magnitude of the difference is the basis on which the degree of hydration is calculated. Apart from the fact that the method involves both the acceptance of the ionic hypothesis and the application throughout of the 1·86 factor in calculating the theoretical depression of the freezing point, it is noteworthy that Jones also leaves out of account in his calculation the effect of hydration on the ionic mobilities and that no allowance is made for polymerisation effects.

Biltz ('Zeits. phys. Chem.,' 1902, vol. 40, p. 185), who recognises that the formation of hydrates in solution may be the cause of some of the abnormal properties of strong electrolytes, has endeavoured to support this view by the argument that as cæsium nitrate—which he assumes is but slightly, if at all, hydrated in solution—depresses the freezing point in accordance with the Ostwald dilution law, it is to be regarded as behaving normally. The electric conductivity of such solutions is not that to be expected from the freezing point results, however ; it therefore follows that conductivity cannot be taken as a true measure of the state of dissociation even in the case of salts which are

The method adopted in Parts I, III and IV of these studies is in principle independent of the assumptions made by those who accept the ionic hypothesis as a basis of calculation. Using cane sugar as hydrolyte, the average values arrived at in the case of a number of chlorides and nitrates appear to be such as are to be expected; the fact that somewhat lower values are obtained with the aid of methylic acetate can be accounted for without difficulty, as already pointed out. It was our intention to discuss our results in connection with the observations of previous workers, especially with reference to the influence of salts and certain non-electrolytes on the solubility of various gases; in this we have been somewhat anticipated by Philip, who, in a recent communication to the Chemical Society,* has developed the method of calculating the degree of hydration of a salt from existing data as to the influence of salts on the solubility of gases.

Although no attempt had been made previously to deduce hydration values from changes in solubility, Setschenow,† Tilden‡ and Rothmund§ had contemplated the possibility of explaining the diminution in solubility of non-electrolytes as a consequence of the diminution in the amount of free water by the fixation of water by the dissolved salts. Jahn,‖ moreover, had foreseen the importance of referring the solubility to the weight of solvent used instead of to the volume of solution. Philip has only called attention to a few cases of close agreement—but it will be seen on reference to Table I, in which the results deduced from the various available observations are collected together, that the agreement is far from being close in many cases. In some cases, doubtless, the determination is affected by relatively large experimental errors, as, for example, Braun's determinations made with nitrogen; Euler's determinations may also be regarded with doubt in view of the use of an unstable substance such as ethylic acetate. The values deduced with the aid of carbon dioxide excite the suspicion that some carbonate may have been formed; the values obtained with thiocarbamide and salicylic acid are open to a similar criticism. In fact, few of the values to the right of the nitrous oxide column command confidence.

not hydrated. Taking the cases of sodium and potassium chlorides—which do not obey the dilution law either as regards freezing points or conductivity—and assuming that they are dissociated to about the same extent as cæsium nitrate, Biltz calculates that the former can be associated with from 19—26 and the latter with 15—24 molecules of water, according to the concentration of the solution; these results are altogether different from those arrived at by Jones.

* 'Chem. Soc. Trans.,' 1907, vol. 91, p. 711.
† 'Mém. de l'Acad. de St. Petersb.,' 1875, vol. 22, p. 6.
‡ A lecture delivered to the Bristol Naturalists' Society, February, 1878, Chemical Society's Pamphlets.
§ 'Zeits. physik. Chem.,' 1900, vol. 33, p. 401.
‖ *Ibid.,* 1897, vol. 24, p. 114.

Prof. H. E. Armstrong and others. [June 20,

Table I. Average Hydration of Salts in Solutions of gramme-molecular Strength.

The values in the other part of the table are both rational and in agreement with those given in the first column, except in the case of the ammonium salts, certain nitrates and the acids.   An explanation has already been advanced of the low values obtained with the aid of methylic acetate in the case of certain chlorides and nitrates; to account for the irrational values given by the acids and in some cases by ammonium salts, it appears necessary to suppose that these exercise a specific solvent influence in presence of water.   Setschenow has shown that carbon dioxide is about equally soluble in sulphuric acid and in water; the monohydrate $H_2SO_4.H_2O$, however, is a less effective solvent than either of its constituents separately and it is the mixture which has the minimum solvent power.   This observation shows clearly both that acids can act as solvents of gases and that the association of water with another substance may lead to a diminution in its solvent power.

Taken as a whole, the outcome of the comparison of the values arrived at in various ways is very striking; it is certainly remarkable. that it should be possible to deduce the degree of hydration of a salt from the diminution in solubility of a gas such as hydrogen, which dissolves only to the extent of 13 molecules per 1,000,000 molecules of water.

Such a result, taken in conjunction with the conclusions deduced from our hydrolytic studies, lends support to the view that solubility is to be regarded as a chemical phenomenon, as a manifestation of chemical affinity, even in the case of gases.   If it be supposed that the gas molecules merely become interposed in the free spaces between the solvent molecules, it is to be expected that equal numbers of molecules would dissolve and that, within limits, the solubility would be independent of the nature of the gas.   Again, if the molecular interspaces are limited in volume, some relation should obtain between the molecular volume of a gas and its solubility: gases of low molecular volume should dissolve the most readily.   The facts do not fit in with either view* (Table II).   The great difference in solubility between ethane, ethylene and acetylene, is especially remarkable, the solubility increasing to a marked extent in passing from the saturated paraffin hydrocarbon to the unsaturated olefine and to an altogether extraordinary extent in passing to the still less saturated acetylene.†

* Jahn (' Zeits. phys. Chem.,' 1895, vol. 18, p. 1) has suggested that the decrease in solubility should be proportional to the amount of surface covered by the solute.   Drude and Nernst (*ibid.*, 1894, vol. 15, p. 79) consider that when ions are present the water is compressed by electrostriction.

† In this behaviour of the unsaturated hydrocarbons there is, perhaps, foreshadowed the altogether astonishing power possessed by charcoal—doubtless an ethenoid form of carbon—of absorbing gases at low temperatures which has been disclosed by Dewar's remarkable observations.

Table II.

Gas.	Molecular weight.	Solubility at 25°.	Molecules per 1,000,000 molecules of water.
		c.c. per litre.	
He	4	13·71	9·9
N₂	28	14·32	10·3
H₂	2	17·54	12·7
CO	28	21·42	15·5
O₂	32	28·31	20·4
CH₄.............	16	30·06	21·7
A	40	34·70	25·6
C₂H₆	30	41·04	29·6
NO	30	42·23	30·5
N₂O	44	59·42	42·9
C₂H₄	28	108·0	78·0
C₂H₂	26	930·0	671·0

The solvent power of water for gases, etc., is modified by dissolved solids presumably in a variety of ways: (1) by the combination of water with the solute and the consequent diminution in the amount of free water; and (2) by the change in the equilibrium $(H_2O)_n \rightleftharpoons nH_2O$ conditioned by the presence of the molecules of the solute, whether hydrated or unhydrated; the extent to which the gas is soluble in the dissolved substance or its hydrate is another influence to be taken into account; changes which the dissolved salt itself undergoes in its state of molecular aggregation in consequence of the inter-position of the neutral molecules, when these are sufficiently numerous, will also affect the equilibrium. These various influences may come into play to counteract one another; consequently, the values obtained cannot be regarded as more than approximations.

The problem before us is to separate the cases in which there is minimum interference with the first-mentioned factor. Taking into account the low hydration values deducible from Knopp's determinations of the solubility of hydrogen in presence of potassium and ammonium nitrates, it appears that hydrogen cannot be used safely in all cases. The determination of the effect produced by neutral salts on the hydrolysis of cane sugar appears to be the most likely means of arriving at probable values—but even the values thus deduced must be regarded as minima, inasmuch as it must be supposed that the acid to some extent combines with the hydrolyte and that when the salt is added it may compete with the acid and alter the proportion of active acid as well as interfere mechanically with its action.*

It can scarcely be doubted that the forces at work in solutions are too

* Cf. IV, above.

complex in character to be expressed as simple mathematical laws. The fact
that water is itself a complex material, which varies greatly in composition as
the conditions are changed, has been left almost wholly, if not entirely, out of
account in discussing electrolytic and hydration phenomena ; and far too little
attention has been paid also to the existence of salts in solution in various
states of molecular aggregation.

The discovery of liquid crystals and the observations of Miers and his
co-workers on the separation of solids from solution in the absence of nuclei
capable of determining crystallisation, as well as the peculiarities manifest
in saturated solutions such as are referred to in No. II of these studies, all
afford indications of complexities which must not be omitted from considera-
tion in dealing with solutions.

The average extent to which a salt becomes hydrated is obviously more or
less dependent upon the amount of water available ; this is clearly brought
out in Table III, in which the values are given which may be deduced from
various solutions of sodium chloride.

Table III.—Average Degree of Hydration of Sodium Chloride at various
Concentrations.

Criterion.	Hydrolysis of cane sugar. (Caldwell.) 25°.	Solubility of nitrous oxide. (Roth.) 25°.	Solubility of hydrogen. (Steiner.) 15°.
5 normal	9·6 .	—	7·5
4 „	—	—	8·4
3 „	11	—	9·5
2 „	—	—	10·4
1 „	13	12	11·2
0·5 „	—	13·6	
0·25 „	—	17·4	

As the results obtained by the cane sugar method apply to weight-normal
solutions and those obtained by the solubility method to volume-normal
solutions, the values are not strictly comparable. The agreement appears to
be closer when the results are expressed in terms of the number of molecules
of free water present per equivalent of hydrate (Table IV); to obtain these
values, it is assumed that the cane sugar and the chlorhydric acid appropriate
between them $15H_2O$, leaving $\dfrac{1000}{18} - 15 = 40$ at the disposal of the
salt. If the average hydration and the concomitant free water are expressed
as co-ordinates, it becomes evident that the hydration value at infinite dilution
will probably not exceed $20H_2O$.

Table IV.—Equilibrium between hydrated Sodium Chloride and free Water.

Sugar hydrolysis. (Caldwell.) Weight-normal solutions at 25°.	Solubility of hydrogen. (Steiner.) Volume-normal solutions at 15°.
5N......... $NaCl\ 9\cdot6H_2O \rightleftharpoons 8H_2O$ 3N......... $NaCl\ 11\cdot0H_2O \rightleftharpoons 13H_2O$ N......... $NaCl\ 13\cdot0H_2O \rightleftharpoons 40H_2O$	5N............ $NaCl\ 7\cdot5H_2O \rightleftharpoons 2\cdot9H_2O$ 4N............ $NaCl\ 8\cdot4H_2O \rightleftharpoons 4\cdot7H_2O$ 3N............ $NaCl\ 9\cdot5H_2O \rightleftharpoons 8\cdot2H_2O$ 2N............ $NaCl\ 10\cdot4H_2O \rightleftharpoons 16\cdot5H_2O$ N............ $NaCl\ 11\cdot2H_2O \rightleftharpoons 43\cdot4H_2O$

Even the values in Table IV are not strictly comparable, as they refer to different temperatures. The influence of temperature is well brought out in Table V, deduced from Roth's observations on the solubility of nitrous oxide.

Table V.—Hydration of Sodium Chloride in volume-normal solution of gramme-molecular strength.

Temperature.	Hydration.
25	$NaCl\ 12\cdot0H_2O \rightleftharpoons 42\cdot4H_2O$
20	$NaCl\ 12\cdot3H_2O \rightleftharpoons 42\cdot2H_2O$
15	$NaCl\ 12\cdot6H_2O \rightleftharpoons 42\cdot0H_2O$
10	$NaCl\ 13\cdot3H_2O \rightleftharpoons 41\cdot4H_2O$
5	$NaCl\ 13\cdot9H_2O \rightleftharpoons 40\cdot9H_2O$

We believe that we are not justified in giving an absolute interpretation of any of the physical properties of solutions which involves the assumption that such properties are the outcome of the simple changes postulated by the advocates of the ionic dissociation hypothesis.

It is only when water is regarded as a changeable and ever changing substance that the full significance of the complex phenomena afforded by solutions becomes apparent. In future it will be necessary to pay more attention to the changes which the solvent itself undergoes and instead of thinking of interchanges as carried out in a mere space to contemplate their occurrence within a medium itself sensitive to every alteration occurring within it. It will be desirable, therefore, to abandon the use of solutions made up to particular volumes—except for analytical purposes—and always to use those instead which contain a known mass of solvent.

In discussing the phenomena of electrolytic conductivity in 1886,* the increase in molecular conductivity which attends dilution was attributed by

* 'Roy. Soc. Proc.,' vol. 40, p. 268.

one of us to the gradual resolution of the more or less polymerised molecules of the salt into simple molecules or monads; conducting solutions were pictured as containing a *composite electrolyte* formed by the association of these monads with the solvent molecules; and the conclusion was formulated that " there is no satisfactory evidence that the constituents of the electrolyte are either free prior to the action of the electromotive force or are primarily set free by the effect produced by the electromotive force upon either member *separately* of the *composite* electrolyte but that an additional influence comes into play, viz., that of the one member of the composite electrolyte upon the other while both are under the influence of the electromotive force. This influence," it was imagined, " is exerted by the negative radicle of the one member of the composite electrolyte upon the negative radicle of the other member."

It is possible now to go somewhat further in explaining the process. The electrolytically effective monads must be thought of as hydrated in some particularly intimate manner, perhaps as hydroxylated, *e.g.*,

$$HCl + OH_2 \rightleftharpoons HCl:OH_2 \rightleftharpoons H\cdot\overset{H}{\underset{OH}{Cl}}$$
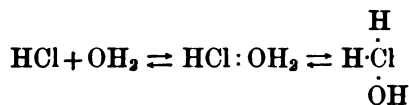
The proportion of the firmly hydrated or hydroxylated molecules in a solution of hydrogen chloride—which probably exists in solution, judging from its gaseous nature, entirely in a monadic form—will depend on the proportion of water present as well as on the affinity of the chloride for water and the correlated stability of the effective hydrate. From this point of view, the differences observed between salts in solution are conditioned both by the different extents to which they exist as polymerised molecules and as monads and by the different extents to which they exist as effectively hydrated monads; the underlying causes of these differences would be the different degrees of affinity inherent in the monads for one another and for water.

The process of electrolysis in a solution, say, of potassium chloride, may be pictured as involving a complete series of interactions among the hydroxylated monads polarised in a manner which may be represented diagrammatically thus:—

$$\begin{array}{l} \quad\quad\quad \overset{\text{H}}{\underset{\displaystyle|}{}} \\ \text{—} \ a \quad \text{K)}\overset{|}{\underset{|}{\text{Cl}}} \\ \quad\quad \overset{|}{\text{OH}} \ \overset{\text{H}}{\underset{|}{}} \\ \quad b \quad \text{K} \ \overset{|}{\underset{|}{\text{Cl}}} \\ \quad\quad \overset{|}{\text{OH}} \ \overset{\text{H}}{\underset{|}{}} \\ \quad\quad c \quad \text{K} \ \overset{|}{\underset{|}{\text{Cl}}} \\ \quad\quad\quad \overset{|}{\text{OH}} \ \overset{\text{H}}{\underset{|}{}} \\ \quad\quad\quad d \quad \text{K} \ \overset{|}{\underset{|}{\text{Cl}}} \\ \quad\quad\quad\quad \overset{|}{\text{OH}} \ \overset{\text{H}}{\underset{|}{}} \\ \quad\quad\quad\quad e \quad \text{K(}\overset{|}{\underset{|}{\text{Cl}}} \longrightarrow \\ \quad\quad\quad\quad\quad \text{OH} \end{array}$$
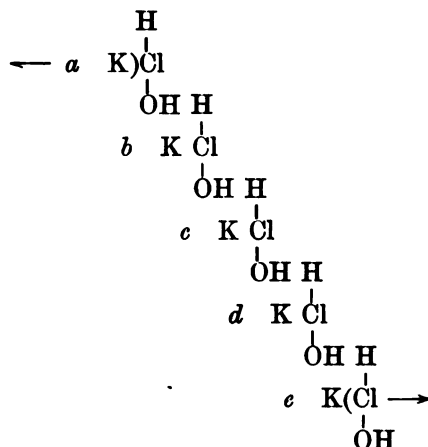
The attraction of the potassium and chlorine ions* to the electrodes may be supposed to determine an alteration of the " affinity " relationships within the molecules such as would permit, in the case of molecule *a*, of the hydrogen ion and the chlorine ion uniting if the OH ion attached to the chlorine ion at the same time were to become associated with the potassium ion of molecule *b*—and so on throughout the chain. The contiguous nascent molecules of hydrogen chloride and potassium hydroxide would interact forthwith. But the substances in solution would be hydrated beyond the hydroxide stage ; and presumably both the hydrogen chloride and the potassium hydroxide would attract more water immediately they were formed. Probably in the rearrangement water would be carried in both directions but in different amounts corresponding to the different degrees of hydration of the two compounds. The mobilities of the " ions " would be more or less affected by and dependent on the extent to which the compounds were hydrated.

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* I have more than once pointed out that the modern use of the term ion—and of its correlative ionisation—is not such as was contemplated by Faraday. It is desirable that some agreement were arrived at and that the conception of dissociation were separated implicitly from both terms. Words are never idle used wrongly, they give rise to false impressions :—" through a very imperceptible but still very dangerous, because continual influence, they do great injury to science by contracting and limiting the habitual views of those pursuing it " (Faraday) ; " those who are not familiar with a subject are very liable to be misled by the deceptive appearance of simplicity conferred by particular names " (FitzGerald). There are now three partially synonymous terms in use, each of which has its special value—the first is atom, the second radicle, and the third ion. The term atom, of course, applies to the elementary, undivided unit ; the term radicle is of more general use, being applicable both to atoms and to groups of atoms which can function as atoms ; both these terms have only a structural significance. The ion, however, is the movable, transferable radicle ; a radicle may be said to be an ion and to be ionised to a particular extent, if it be movable by chemical means to the particular extent to which it is said to be ionised.—H. E. A.

Although the water is thought of as attached only to the negative ion, both ions would appear to be hydrated, on this hypothesis.

The arrangement suggested is but a modification of the Grotthus' chain. It is difficult to avoid the conclusion that the facts on the chemical side are such as require some such explanation of the phenomena, and that we are justified in asking physicists to re-examine the arguments which have led them to take exception to the Grotthus explanation. FitzGerald has already spoken with no uncertain voice and given us his support, in his memorial lecture on Helmholtz. Of late years probably no one has shown greater power of appreciating all sides of the position : his adverse criticism of the dissociation hypothesis is therefore of peculiar value.

The Effect of Pressure upon Arc Spectra. No. I.—*Iron.*

By W. Geoffrey Duffield, B.Sc., B.A.

(Abstract.)

The first part of the paper contains a description of the mounting and adjustment of the large Rowland Concave Grating in the Physical Laboratory of the Manchester University. The feature of this is the stability of the carriages carrying the grating and camera, and the novel construction and attachment of the cross-beam, which secure the absence of any disturbance which might be caused by bending or sagging.

The second part describes experiments made with a pressure cylinder designed by Mr. J. E. Petavel, F.R.S., in which an arc is formed between metal poles opposite a glass window, through which the light is examined by means of the Grating Spectroscope. A system of mirrors allows the image of the arc, however unsteady it may be, to be kept almost continuously in focus upon the slit.

Two sets of photographs of the iron arc in air have been taken for pressures ranging from 1 to 101 atmospheres (absolute), and the results are given below for wave-lengths $\lambda = 4000$ Å.U. to $\lambda = 4500$ Å.U.

I. *Broadening.*

1. With increase of pressure all lines become broader.
2. The amount of broadening is different for different lines, some almost

becoming bands at high pressures, and others remaining comparatively sharp.

3. The broadening may be symmetrical or unsymmetrical; in the latter case the broadening is greater on the red side. ·

II. *Displacement.*

1. Under pressure the most intense portion of every line is displaced from the position it occupies at a pressure of 1 atmosphere.

2. Reversed as well as bright lines are displaced.

3. With increase of pressure the displacement is towards the red side of the spectrum.

4. The displacement is real and is not due to unsymmetrical broadening.

5. The displacements are different for different lines.

6. The lines of the iron arc can be grouped into series according to the amounts of their displacements.

7. Three groups can in this way be distinguished from one another; the displacements of Groups I, II, III bear to one another the approximate ratio 1 : 2 : 4. (The existence of a Fourth Group is suggested by the behaviour of two lines, but further evidence is needed upon this point; 1 : 2 : 4 : 8 would be the approximate relations existing between the four Groups.)

8. Though all the lines examined, with two possible exceptions, fall into one or other of these Groups, the lines belonging to any one Group differ to an appreciable extent among themselves in the amounts of their displacements.

9. The relation between the pressure and the displacement is in general a linear one, but some photographs taken at 15, 20, and 25 atmospheres pressure give readings incompatible with this relation. Other photographs at 15 and 25 atmospheres present values which are compatible with it.

10. The abnormal readings are approximately twice those required by the displacements at other pressures, if the displacement is to be a continuous and linear function of the pressure throughout.

11. On the photographs showing abnormal displacements the reversals are more numerous and broader than they are on plates giving normal values, and there is some evidence in favour of a connection between the occurrence of abnormal displacements and the tendency of the lines to reverse.

III. *Reversal.*

1. As the pressure is increased, reversals at first become more numerous and broader.

2. The tendency of the lines to reverse reaches a maximum in the

neighbourhood of 20 or 25 atmospheres, and a further increase in pressure reduces their number and width.

3. Two types of reversal appear on the photographs, symmetrical and unsymmetrical.

4. Within the range of pressure investigated the reversals show no tendency to change their type.

5. In the case of unsymmetrically reversed lines in the electric arc, the reversed portion does not in general correspond to the most intense part of the emission line, being usually on its more refrangible side.

6. The displacements of the reversed parts of the unsymmetrically reversed lines of Group III are about one-half the displacements of the corresponding emission lines. Indeed, the reversed parts of the lines of Group III fall approximately in Group II.

7. No relation between the order of reversal and the frequency of vibration, such as exists in the spark, has been observed in the iron arc for the ranges of wave-length and pressure examined.

IV. *Intensity.*

1. The intensity of the light emitted by the iron arc is, under high pressures, much greater than at normal atmospheric pressure.

2. Changes in relative intensity of the lines are produced by pressure. Lists of enhanced and weakened lines are given.

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PROCEEDINGS

OF

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Series A. Vol. 79. No. A 534.

MATHEMATICAL AND PHYSICAL SCIENCES.

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